Previous references.
Ed^n 272-09-1

Later references
~~Edn~~ 42-1464 #9)
Edn 62-15 Pts 1-3

1910
(Education)

File No 480-09
Serial Nos 1-7

GENERAL AND REVENUE SECRETARIAT

Serial Nos 1-7

Part B for October, 1910

SUBJECT

Appointment of Mr Frances Usher, B Sc, as Professor of Chemistry, Central College

, the 9 ult of Ed^n, no 11437/819 S 25 5 10 States that Professor Rankin and Dr Fraser have recommended Mr Frances Usher, B Sc for the Chemistry professor's place and requests that his appointment may be sanctioned

From Do, no 11600/837 S 30 5 10 Submits Mr Frances Usher's formal application for the post of the Chemistry Professor together with testimonials etc and also an application from Dr Thomson, Ph D, for the same post

To the Asst Resident, no C 146 S 23 6 10 Applies for the sanction of the Govt of India to the employment of Mr Usher

From Do, no 3978 S 17 10 States that there is no objection to the employment of Mr Usher as Professor of Chemistry

G R S 58

1909 10

GENERAL AND REVENUE SECRETARIAT

(Education)

NOTES

File No 680 ag

FILE HEADING

Appointment of Mr Francis Usher, B Sc, as Professor of Chemistry, Central College -

No	Dated	Received	
Diary No	Enclos	Spare Copies	Serial No

BRIEF ABSTRACT OF LETTER

NOTES AND ORDERS

First sheet

GPB— 0 000—3 4 07

774

Bangalore
9 Ap 10

My dear Sir,

Kindly let me know what progress has been made in the matter of getting down an upto date Professor of Chemistry for the Central College at Bangalore & oblige

Yours Sincerely
sd) T Anandakar

J Weir Esqr Secy

"Copy"

CP
9 Ap 10

D O No. 7848/9

Office of the Inspector General of Education
in Mysore, Bangalore, the 1 April 1910

Dear Sir,

About the new Professor of Chemistry I wrote last mail to Sir William Ramsay asking him to nominate two or three candidates for selection by Government I sent him a copy of the Madras University Calendar and of the Mysore Service Regulations, also a copy of the Government Order appointing Mr Metcalfe I said Government would give the same terms as they gave to Mr Metcalfe except that they would prefer him to have the leave rules of the Mysore Service instead of the Indian Institute of Science at the same time if he could get a better candidate who insisted on the leave rules of the Indian Institute of Science he might send in his application for consideration by Government

I also gave him Mr Metcalfe's address in London and said he might refer any candidate to him for additional information

---

Previous Refs To 7748 9 Apr 10

2 I wrote to Mr Metcalfe asking him to recommend any suitable candidate to apply through Sir William Ramsay, and to give any information to any candidate who applied to him

3 I wrote to Dr Travers and asked him to recommend any candidate to apply through Sir William Ramsay and if necessary to apply to Mr Metcalfe

4 I sent a similar letter to Dr G A Gibson, Professor of Mathematics in Glasgow University who may possibly be able to recommend a good man

All these letters were posted on Thursday night in Bangalore in time for the mail

I have also asked Mr Tait to make inquiries in Edinburgh, where he is going to spend part of his summer holidays

Yours sincerely,

Gwen

Inspector General

To,

T Aranda Rao Esq ,

Dewan of Mysore

Previous Refs To 7748 9 Apr 10

Submitted to His Highness

As the time is fast approaching for the appointment of a Chemistry Professor for the Bangalore Central College, not merely for the lecturing work, but also for the preparation of the plans and estimates for the lecture rooms and the laboratory, I asked Mr Weir for information as to the steps he had taken in the matter I annex his reply which I trust will be found to be satisfactory In a matter like this, it would probably be far better to secure a Professor through well-known agents, as Mr Weir is trying to do, rather than by merely advertising for candidates

2 In this connection I feel it my duty to submit for perusal the accompanying file (Education File No 310 of 09-10) in which the requirements of the Central College are discussed at some length I have not made up my mind on the subjects therein discussed as there are one or two points on which I would probably require further information, and I submit the file now only for information before I formally seek His Highness' orders on the subject My inclinations at present are to agree entirely with

under the opinions of Mr Weir and the Second Councillor I would be very sorry if Geology be dropped as proposed by Mr Tait I would give a great deal to have both Geology and Chemistry That a class for any of these sciences would be small need not be an objection for establishing a chair in that science The smaller a class the greater the attention that can be bestowed on each student and therefore the better the quality of instruction Of course it will not do to have too small a class, but the chances are that, although the classes may be undesirably small in the beginning, they will grow in numerical strength in the course of a very few years, and in a matter like this it is well to look ahead

3 In this connection also I wish to submit for perusal a note which the Second Councillor has just sent up containing proposals for the grant of scholarships to students desirous of going to Madras for taking up the Honours Course

be

P Ramanathan
13 April

14
1058
4

761

Record of Cases submitted for the Orders of His Highness the Maharaja

Subject

Appointment of a Chemistry Professor for the Bangalore Central College

Order

~~KRW~~
15/4/10

Secy
16 Apr 10

Keep confidential after
Intn to CRs
19/4/10

19/4/10

22/4/10

GRS 11]

~~1909-10~~

~~GENERAL AND REVENUE SECRETARIAT~~

(Education)

NOTES

File No 480-09

FILE HEADING

Appointment of Mr Francis Usher, B Sc, as Professor of Chemistry, Central College.

From

The Secy to Govt in Mysore

No 11437/819 Dated 25/5/10 Received 27/5/10

Diary No 8527 Enclos Spare Copies Serial No

As From the Secy to Gov in Mysore No 11437-819, B 25/5-10 8498

~~BRIEF ABSTRACT OF CONTENT~~

States with Reference to this office letter No 307-09-2 B 29/8/10 that Professor Ramsay and Mr Travers have recommended Mr Francis Usher, B Sc., for the Chemistry Professor's place and requests that his appointment may be sanctioned

NOTES AND ORDERS

The terms of the appointment are the same as those offered to Mr Metcalfe except as regards the leave rules viz

(1) Pay Rs 500-50-1000

NOTES—First sheet

GPB—0000-3 1 07

Serial No

(2) Appointment to be on probation for 5 years at the end of which period it will be open to either part to terminate the Contract

(3) Pension to be regulated by the Mysore Service Regns

(4) Single first class passage to be paid for his journey from England to Bangalore at the commencement of his Service and also at the end of 5 years of the Contract is terminated then

(5) Travelling allowances to be regulated by the Rules applicable to European Officers in the Mysore Service

2 As regards leave Rules, Mr Wen says that the question may be decided after Mr Usher joins his appointment. In the case of

Serial No

Mr Metcalfe the leave Rules are guided by those applicable to the Professors of the Indian Institute of Science These Rules give 3 months' Continuous Vacation to a Professor. Under the new University Regns, colleges will be closed for about 3 months in Summer. Therefore there will be no advantage to the new Professor in making the Institute Rules applicable to his case. The Govt therefore states that the matter may be left open till he puts his appeal

3 All the particulars required for applying for the Sanction of the Govt of India are not furnished.

Submit for orders

Mm 20/5/10 (Secretary) 20/5/10

4 Judging from Sir Ramsay's & Dr Mukerji

GPB— 000—27 4 9

Serial No

letters in Usher seems to be a good selection for the post of Chemistry Professor. If his nomination is approved full particulars regarding him may be called for & a formal application made to the Govt for the sanction of the post of 2nd Chemist & Demonstrator

Chy 28/5/10

The DO correspondence & Govt orders on the subject are put in Flag D

Serial No 2

From the Jt Sec to Govt

No 11600/B37 dt 30/5/10

Submits in continuation of his Recommendation for appointing Mr Francis Usher as Chemistry Professor, his formal application for the post together with testimonials etc and also an application from Dr Thomson, Ph D., for the same post

5 Dr Thomson is now Asstt in the Senior Chemistry Deptt of the University of Glasgow and is 31 years old — Mr Usher is ~~nearly~~ 24 years old The Jt Sec states that Sir William Ramsay recommends the selection of Mr Usher as his ~~of~~ work shows greater originality

8535 b

GRS 12]
General and Revenue Secretariat

File No 480 of 1909-10

Serial No

6 The previous papers have been submitted to the 2nd Councillor on 28/5/10.

Hm Song 31/5/10

2nd Councillor

31/5/10

3941

7 The DG's recommendation about Mr Usher may be accepted

Dewan

2/6/10

6479
4-6-10

8 Please circulate to the 1st Councillor

4 June 10

9 Circulate

5/6/10

4404
7 6 10

From all accounts Mr Usher would be an acquisition to the Central College He may be appointed Professor of Chemistry

7/6/10

6516
8-6-10

NOTE—Contn sheet

GPB—5 000—27 4 9

G R S 12]
General and Revenue Secretariat

File No of 190

7

Serial No	
11	Dewan CRB 7/6/60

NOTE—Contn h t

G1 b—5 00)—27 4 9

C 456
6 6 10

GENERAL AND REVENUE SECRETARIAT

Council Matter

SUBJECT

Appointment of Mr Frances Usher B Sc
Professor of Chemistry in the Central College

CIRCULATED TO COUNCILLORS

By Order

6th June 1910

C S Balasundaramayya
Offg Secretary to Government

C P Tuttanna Chetty Esq
First Councillor

H V Nanjundayya Esq M A M L
Second Councillor

Opinion recorded by 2nd Councillor

Submitted to His Highness

12

D

Paper under disposal

In continuation of my note dated 13th April 1910 reporting the steps taken by the Inspector General of Education in the matter of appointing a Professor of Chemistry for the Central College, I submit herewith Mr Weir's final report in the matter

2) Sir W Ramsay, to whom the Inspector General of Education had written on the subject, has recommended for the place Mr F L Usher B Sc (London) He is 24 years of age and seems to have had a brilliant career, and to have done considerable original research work, and to be otherwise possessed of qualifications eminently suited for a Professorship in Mysore The quotation from Sir William's letter, contained in Mr Weir's communication dated 25th May, is worth perusal The only other candidate who has applied is Dr David Thomson of Glasgow University He also seems to be a good man, but Sir W Ramsay considers that Mr Usher's work shows greater originality, and he is 7 years older than Mr Usher

Paper under disposal

3) Both the Councillors are of opinion that

Mr Usher may be appointed Professor of Chemistry This may be sanctioned, and Mr Usher may be asked to hold himself in readiness to start as soon as the sanction of the Government of India to his engagement is obtained and communicated to him

4) The terms of the engagement, which are the same as those for Mr Metcalfe, except the leave rules, will be as follows -

(1) Pay Rs 500-50-1000

(2) The appointment to be on probation for 5 years at the end of which period it will be open to either party to terminate the engagement

(3) Single first class passage and railway fare to be given from London to Bangalore, and if the engagement is terminated by either party at the end of 5 years, for the return journey also

(4) The leave rules to be those contained in the Mysore Service Regulations (In Mr Metcalf's case the leave rules are the same as those for the Professors of the Indian Institute of Science)

(5) Travelling allowances, the same as for Educational officers of class Aii for the first five years and of class A i thereafter

(6) Pension according to the rules of the Indian Educational Service

* Or more correctly speaking the pension rates will be under Imperial Regulations, the leave being under the Mysore Regulations

24 June

Record of Cases submitted for the Orders of His Highness the Maharaja

8 6-10
1273

Subject

Appointment of Mr Francis Usher B Sc as Professor of Chemistry in Central College Bangalore

977

13

Order

KRW
10/6/10

14

Secy
Early
Sir
N Prucco

15 Publish draft to Secy
CM
12/6/10

(Please see note attached)
12/6/10
13/6/10

Serial No

14 We passed a general order that no special conditions shd be introduced in such cases without Govt sanction If I remember correctly, both leave & pension were to be regulated by the Mysore Service Rules Please put up that order

15 It was precisely to get rid of the inconvenience of referring to India Rules that that order was made Please elucidate this matter before issuing the order of appt.

12/6/10

Urgent

16 A memorandum has been issued stating that in the case of future employment of European officers, the Mysore Service

Serial No

as that fixed for the officers of the Indian Edl Service - Submitted with a draft letter to the Residency

KW 18/6/10

Mr. Ushis pension to is proposed to be regulated by the Mysore Service Regns according to the terms offered to him by Mr. Wem. through in sub-para (6) of para 4 of the Dewan's note the Dewan's note to it is proposed to be regulated by the Rules for the Indian Edl Service.

and mentioned in para 4 of the Commission note to it

KW 18/6/10

2nd Counsellor

18/6/10

16 I have instructed the draft to the Residency. The Pension should be accd. to the Mysore Service Regulations. The rules of the Indian Edl Service in the Dewan's note is apparently a mistake

18/6/10

Dewan

18/6/10

664/20-6-10

[R.S 12]
General and Revenue Secretariat

GOI File No 480 of 1909-10

Serial No

Vide addition made in the Statement accompanying the letter regarding the rate of exchange of pension This is what is meant in sub para 6 of para 4 of the Submission note

2 After issue of the letter the Dy of Education may be asked to communicate with Mr Ledger and to request him to hold himself in readiness to start as soon as the sanction of the Govt of India is received

21/June/10

19
1) Issue
2) Intimation to submit to 2nd Cr

21/6/10

20 To the First Asst Resident
No C146 dt 23/6/10

Applies for the sanction of the Govt of India to the employment of Mr Usher.

21 Submit with a draft letter to the Dy Sec of GOI

23/6/10 2nd Counsellor)

23 6 10

GPB— 000—27 4 9

Serial No

23 In our office memo of 4 Feb 1910, it is stated as follows "If however in very exceptional cases, it is considered necessary to make other rules applicable, the deviations from the M S Regns proposed should be fully set forth for the consideration of Govt ~~in the~~, and the Govt in the adm^ve department should consult the H Br before the proposals are approved" This was duly communicated to the Dy of Edn.

Art 523A of the M-S Regns makes all pensions payable in Rupees in India and if in exceptional cases, payments are made in England, they are convertible at the current rate of Exchange This article applies to all officers who entered the service prior to 21 Nov 1905

24 To make the pension payable at 1s-9d acc^g to Br Indian rules is a very material deviation, enhancing the pensionary charge by about 30 p.c The matter was not placed before Govt in the manner directed by the G.O quoted

GPB—5 000—27 4 9

Serial No

above, I ~~do not~~ think therefore that Mr Weir was not in order in offering any exceptional terms, without the sanction of Govt. I may add that though the fr appointing Mr Metcalfe contains a statement about the rate of exchange, the letter to the Residency & the statement appended thereto about the terms do not contain this concession

(25) The only appreciable difference between the Mysore & Indian Regulations applicable to this case is this — of the rate of convertibility of the Rupee. It was ~~only~~ just in that point that the ~~[illegible]~~ discussion occasioning the Govt Memorandum of Feby last, ~~to~~ had been raised by me & in my humble opinion, the said order would be altogether ignored by the introduction of this concession, and as far as I see

G R S 12]
General and Revenue Secretariat

Gen. File No 450 of 1909-10

Serial No

from the papers, it is a needless sacrifice

(25) I regret therefore I have again to trouble the Dewan with this matter, but if he still is of opinion that the concession is absolutely necessary to secure the services of a good Professor, I shall have no objection to its being granted as proposed. I would however suggest that the DG's attention may be drawn to this omission. 26/6/10

Seen to take the order of Govt. before offering the terms in this case

26/6/10

(26) Sub to Dewan

6683
28/6/10

CSS
27/6/10

(27) Seen —

Write my DO to Mr. Irwin of 30 June when reply of 1st July —

I am afraid it is too late to raise the question of the rate of exchange

* Please see pages 30-34 of the Notes

NOTE—Continue sheet

Serial No.

for leave allowances & pension —

28 With his first letter Sir W. M. Ramsay Mr Weir sent a copy of the Mysore GO containing the terms of Mr Metcalfe's appointment. In this GO the terms relating to the rate of exchange are unmistakeably given —

29 In the minutes of Councillors who led up to the Mysore "Note B" Mr Ushers selection was approved". It follows that the terms offered to and accepted by him were also approved.

30 I don't think that we can now revise the same —

31 Mr Weir says he has no letter of mine authorising any departure from the Mysore Leave Regulations in regard to the point now under discussion. But I have a recollection that he spoke to me before writing to Sir Wm Ramsay and that I agreed to the terms to be offered being identical with those on which Mr Metcalfe had been entertained. There was a talk about the leave being regulated as it is in the case of the

Serial No

of the Professors of the Indian Institute of Science, the more especially as leave to go to ~~England~~ Europe in the case of these Professors meant not merely a holiday but an opportunity for refreshment of their knowledge of the sciences so as to bring it up to date — This accounts for the question whether the leave rules shd be according to the Mysore Leave Regulations or according to the Indian Institute of Science being yet kept open —

32 Indeed, if the question of the rate of exchange had been raised in express terms, I think we should have thought it expedient to place the new Professor of Chemistry on the same footing as the Professor of Physics —

33 In these circs I wish to know whether the 2d Councillor desires to press the point now raised by him —

2 July 10

34
Sub to 2nd C

C 583
2/7/10

$20 \times 5000 =$

100000

Serial No

5

35 When there is an express order of Govt that deviations should be specially reported, I cannot see the force of any estoppel against Govt or the members thereof, that they did not discover that Mr Metcalfe's terms included payment of pension at 1S 9D a rupee As far as I can recollect, Mr Metcalfe's file was not put up I assumed that the terms ~~as~~ were correctly reproduced in the office note (P 2) where it is stated that one of them was

"3) pension to be regulated by the Mysore Service Rules"

36 The difference came to light for the first time when I read the Dewan's note referring to the Indian Regulations, and I at once noted my view upon it

37 Mr Weir's d O letter shows that he did not mean to offer any terms not included in the Mysore Service Regulations As the terms have not been accepted finally by Govt, and as the I G

Acting of the GOI, Mr Metcalfe's case was put up with his letter to Mr Ramsay. The GOI quite replied on the point
[illegible]
7 Jul, 10

No

of Education acted ultra vires in offering any more advantageous terms than those of the 2nd Regns, it seems to be by no means too late to correct the terms & ask the Applicant whether our terms suit him As it makes a difference of more than 100Rs in pension monthly to an officer ~~of lately~~ having a right to retire at about 50 yr. of age, the ~~loss~~ extra cost to Govt is by no means negligeable

38 However in deference to the views expressed by the Dewan I do not wish to press my objection. ~~if he does not see fit to reconsider his position~~

2/7/10

2/7/10

39 Dewan

40 Circulate to Committee for opinion

2/7/10

6755
27-10

13
4710

Serial No 41

Mr Meer has frankly admitted that he was not aware of the difference in the matter of pension exchange when he wrote his letter of the 5th April 1910 to Sir William Ramsay & offered the same terms as this sanctioned to Dr Metcalf. At all events he appears to have obtained the oral sanction of the Dewan to this proceeding and he further confirmed it in his DO of the 11th idem to the Dewan. So far Mr Meer's action was quite above board. The terms offered to & accepted by Mr Usher were unequivocal and I doubt if we should be justified in repudiating them now. In fact, if the question of pension exchange had been definitely raised I am not sure that we would have treated the case differently from that of Dr Metcalf.

GPB—35 000—27 4 0

Serial No

As stated by Sir William Ramsay it is difficult to induce men of real scientific ability to come out to India and I do not think we could have got Mr Usher on less favorable terms Mr Meir's letter to govt left no room for doubt as to the terms offered & in accepting those terms I had no idea that they differed from those of Dr Metcalf's engagement

42 Under the circumstances stated in the Dewan's note of 2d July current and the explanation given by Mr Meir, the engagement of Mr Usher may be accepted as an accomplished fact The Residency too has been addressed in the matter

KVR
4/7/10

43

Dewan

5/7/10

PTO

Serial No

4 From the First Asstt to the Resident in Mysore
No 3978 dt 1/7/10

States that there is no objection to the employment of Mr Usher as Professor of Chemistry on the terms proposed

44 The file on the subject with the minute of the Hon Commissioner is submitted to the Dewan.

km
4/7/10 Secretary)

km 5/7/10

6774
6-7-10

45 Approval order passed may now give the Dy C asked to get down Mr Usher

Attd 6 July 10

46 Put up draft (carefully state the terms of employ)

km 6/7/10

47 Draft submitted

km
5/7/10 Secretary)

km 5/7/10

Note—Contn sheet

Serial No

46 Draft submitted to 2nd C

CB
8/7/10

49 The draft is approved Issue after submission to the Dewan

9/7/10

50 Dewan

CB
11/7/10

Draft approved

6854
11/7/10

5 To the Govt of Madras
in Council
G.O. No C 23-24 Dt 13/7/10
Sanctions the appointment of Mr Usher as Professor of Chemistry in the Central College

51 To Mr V for note & return

29/7/10

noted & returned.
1-8-10

R 13 0/10-11
29/7/10

26

To

The Dy Sec of Education

Bangalore

Primary

Order sanctioning

Mr Ushers appointment

issued ~~posted~~. Please communicate

to him tomorrow's mail

CBB

Dy Sec

Issued

13/7/10

Serial No

From the Dy Gl of Edn
No 3302/225 dt 28/9/10
Reports that Mr Usher joined his appt as Professor of Chemistry on the forenoon of Sunday the 25th Sept 1910
52 Submitted with a Draft Notfn.

Secy
3/10/10

Secretary)

3/10/10

53 2nd er

3/10/10

54 Has not the appointment been already gazetted? If so, is it usual to gazette joining in such cases? If the not^n has been issued, is it not only the appt^n that need be notified?

4/10/10

55 Publish alternative notn

5/10/10

G R S 12]
General and Revenue Secretariat

File No 480 of 1909-10

28

Serial No

578

Alternative draft Sanctioned

Thw 5/10/10 (Secretary)

6/10/10

The alternative draft now put up may be approved Notifications of appts were made in the cases of Messrs Metcalfe, Reddy & Subba Rao.

2nd

8/10/10

Inclusive' seems unnecessary It is enough if the Compt^r knows that charge was assumed in the forenoon

8/10/10

Issue

8/10/10

To Compiler Mysore Gazette No 3385 & 18 10 1910

Published at pp 421 & 10 10 1910

Forwards for public Not appointing Mr Frances Usher, B Sc as Professor of Chemistry in the Cent coll Bangalore with effect from the 25 9 1910 forenoon

To Compt No 33869 & 18 10 1910

Forwards a copy of the above and states that Mr Usher entered upon his duties in the forenoon of 25-9-1910.

NOTE—C tn sh et

CPB—50 000—12 8 10

GPS 15]

Facing sheet for Cases included in the schedule appended to Notification No 36 of the 8th August 1907

GENERAL AND REVENUE SECRETARIAT

Subject— Appointment of Mr Frances Usher B Sc as Professor of Chemistry in the Central College

	Date	Initial of Officer himself or responsible Deputy
Received in the Secretariat	27 5 60	
Submitted to Secretary	31 5 60	
Submitted by Secretary to ~~Dewan or~~ Councillor in charge	— do —	
Returned to Secretary	2 6 60	
Circulated by Secretary for Council	6 6 60	
Forwarded by 2nd Councillor	2 6 60	
Forwarded by Councillor		
Received in Secretariat		
Considered in Council		
Submitted to the Dewan		
Submitted to His Highness		
Orders passed by His Highness		
Final Orders issued		
Circulated to Councillors		
Passed on by the Councillor		
Returned to Secretary by Councillor		

30

Mysore

D O No. 962

30th June 11

Urgent

My dear Sir,

In regard to the terms proposed for the appointment of a Professor of Chemistry for the Central College, objection has been taken to allowing the rate of exchange for leave allowances and pension on being regulated by the ~~and~~ Indian Educl. Service Rules. This has been allowed in the case of Mr Metcalfe, but it is pointed out that it is at variance with the terms of the official memo No 6761/85 dt 272-09-1 of 4th Feby 1910, under which the Mysore Service Rules are to be wholly applicable in the case of all appointments subsequent to that date, and if in any ~~deviations~~ ~~departure is taken~~ exceptional case it is considered necessary to make this rule applicable the deviations from the Mis Rules should be-

set ~~forth~~ forth for the consideration of the Govt

I shall therefore be obliged by your kindly letting me know whether the offer of terms similar to those given to Mr Metcalfe, which are not entirely governed by the Nat Regs, ~~by~~ ~~[illegible]~~ ~~the~~ was made with the ~~sanction~~ ~~of~~ approval of the Govt. If there is any so letter from me authorizing this shall be glad of a copy

Yours truly

[signature]

Wembley Mot
U.S. Ger

118

+T
32-34

32

DO No 7/1096

Bangalore
July 1 1910

Dear Sir,

In regard to the terms proposed for the appointment of a Professor of Chemistry there was no D O letter from you authorising any departure from the Mysore Service Regulations I informed you by D O about the middle of April of what I had written to Sir Wm Ramsay on April 5th but I do not seem to have kept a copy of this letter

I was under the impression that the rates of exchange for pension and leave allowances are the same in Mysore as in British India and that the only departure

from the Mysore Service Regulations as the agreement with Mr Metcalfe is in the matter of the leave rules I wrote the letter in camp Sir Wm Ramsay and was misled by the letter from Govt to Sir Wm Ramsay in Jan 1908 asking him to look out for a Professor of Physics, in which it is stated that the leave and pension rules in Mysore are the same as in British India I knew that this is not quite accurate in some other particulars but as this letter to Sir Wm Ramsay was written shortly after the question of pension exchange was settled it did not occur to me that it could possibly be wrong, and I thought that it was advisable in writing to Sir Wm Ramsay to

+T
32-34

say as little as possible about the differences 34

I need hardly say that if I had noticed that there is any other departure from the Mysore Service Regulations in the contract with Mr Metcalfe, I would have asked for Govt orders before writing to Sir Wm

I was unable to find out in the office today what the difference is but on hearing from you I shall be glad to write and explain to Sir Wm Ramsay

Yours sincerely
J Weir

I am under Rao Sahib C Q Z
Dewan of Mysore

Ed 480 ~~[illegible]~~
— 5 C 1

8 8527

Edn 81]

OFFICE OF INSPECTOR GENERAL OF EDUCATION IN MYSORE

No 11437/819 Enc / Bangalore 25 May 1910

From

J Weir Esq , M A ,
~~H J BHABHA Esq M A~~

Inspector General of Education in Mysore

To

C S Balasubramaram Iyer Esq , B A ,
Offg Secretary to the Government of H H the Maharaja
of Mysore, General and Revenue Departments, Bangalore

SIR

With reference to your No 8456 / Ed 301-09-2 dated 29th Ma 1910, I have the honor to recommend the appointment of Mr Francis Usher B Sc , as Professor of Chemistry in the Central College Mr Usher studied at the University College, Bristol, where he took his degree of B Sc , with honours in Chemistry in 1906 as an external student of the University of London In 1908 he entered Sir William Ramsay's Laboratory, University College, London as an internal student of the University He is spoken of very highly by Sir William Ramsay who writes as follows -

" I am in receipt of your favour of the 5th instant, in which you inform me that the Mysore Government wishes me to recommend two or three qualified men for the Chair of Chemistry in the Central College, Bangalore

" I have made inquiries, and the result has been that Mr. Francis Usher B Sc , has expressed his willingness to be a candidate I may say that it is somewhat difficult to induce a young man of ability to leave England, and I think it is very fortunate that Mr Usher has made up his mind to apply

" Dr Morris Travers can tell you much more than I can of Mr Usher's early work, for he was one of Dr Travers' students at Bristol When he came to my laboratory, more than two years ago, he had already made a name for himself by his investigations on the first changes occurring in plants by the assimilation of carbonic acid and water from the atmosphere Since being here, he has carried out a first-rate piece of work of his own on the atomic weights of nitrogen and sulphur, obtained by the analysis of sulphide of nitrogen, a substance which he was the first to prepare in a pure state This work, I feel sure, will be regarded as the final say on the matter

" Mr Usher has also helped me in my work on the newly discovered radioactive substances, and has investigated the action of one of them on ammonia The paper has been published in the transactions of the Chemical Society, and again it is exhaustive and complete In short, whatever Mr Usher does is well done, he is positively a genius in his own way, and that is acknowledged by all my Assistants and by my Colleague, Professor Collie

" As I have a little knowledge of Indian conditions, having visited India in 1900-01, I may add some remarks as to Mr Usher's suitability for the work which he will have to do He is a good expositor, for he thinks clearly He speaks carefully and slowly and is a good teacher He has the power of interesting others in his subject I have great hopes that he might infect some of his senior men with his enthusiasm, and that is what is wanted in India men who will advance their subject Practically, no real advance in Chemistry is made in India and I can not help thinking that that is due to the want of inspiration of the teachers, who have hardly ever known what research is before being appointed to chairs I am sure that Mr Usher would justify his appointment in this respect, and that he would at the same time conduct all routine work efficiently

" Mr Usher could leave England within any reasonable time, so as to superintend the erection and equipment of the laboratories

" I ought to mention that his health is good, he is a wiry, though not a robust man He is quiet in his manner, but he has great

decision of character From this point of view, he is all that could be desired

" I have not made further inquiries, for I am satisfied that it would be difficult to find a man, not already in an established position, with Mr Usher's capabilities But should you wish, I can make further inquiries

Dr Travers writes -

" I hear that Ramsay has sent in the name of F L Usher for the Chemistry post He was one of my Bristol men, and the brightest student I ever had to deal with He is very much the gentleman, and an excellent lecturer and writer, besides being brilliant at research The Central College is in luck "

Mr Metcalfe had an interview with Mr Usher and writes of him as follows -

" Mr Usher was a student of Dr Travers at Bristol, and has recently been working in Sir William's laboratory at University College He seems to have done some good original work, and to have the reputation of being a first rate man in the laboratory Personally he appears to be a quiet, well bred young fellow, and likely to make a very agreeable colleague He must have been with Travers at the time of reorganisation of the Chemistry teaching at Bristol, and should therefore, be well acquainted with modern methods of management of teaching laboratories "

There are no other candidates for the post although Mr Metcalfe informs me that a Glasgow man wrote to him asking for some particulars However Mr Usher's testimonials are so good that I think there should be no hesitation in appointing him

As regards the terms of the appointment I enclose a copy of the letter which I wrote to Sir William Ramsay asking him to select some candidates for the post The terms offered to Mr Usher should be the same as those offered to Mr Metcalfe with the exception of the Leave Rules I said that Government would prefer his leave to be regulated by the Mysore Service Rules rather than by those of the Indian Institute of Science as in the case of Mr Metcalfe At the same time I said that if Sir William Ramsay could get a better

man who would take the leave rules of the Indian Institute of Science a sine qua non, he might send in his application for consideration by Government As nothing is said by Sir William Ramsay on this point, it would be better, in order to avoid the possibility of any misunderstanding, to leave the matter open until Mr Usher arrives and give him some little time to make up his mind whether to accept the Mysore Rules or the Indian Institute Rules

The main reason for giving the Institute Rules to Mr Metcalfe was that these rules give a professor three months' vacation every year, and in this way he can keep himself in touch with scientific progress by frequent visits to England But when the new curriculum of the Madras University comes into force the ordinary vacation of the Central College will be very nearly, if not quite, three months so that there will be very little advantage gained by selecting the Institute Rules On the other hand the Institute Rules seem to be very much harder on a professor in case of illness, and if Mr Usher prefers to run the risk of accepting the Institute Rules, the advantage will be on the side of Government

I have the honor to be,

Sir,

Your most obedient servant,

Inspector General

Office of the Inspector General of Education

No 10014-17/1074 in Mysore, Bangalore, 5 April 1910

From,

J Weir Esq , M A ,

Inspector General of Education in Mysore

To,

Sir William Ramsay,

Professor of Chemistry, University College,

London

Sir,

I am directed to inform you that the Mysore Government is going to create a new appointment of Professor of Chemistry in the Central College, Bangalore The Mysore Government will feel obliged if you can kindly recommend two or three qualified men from whom a selection may be made

2 The new Professor will be given the same terms as were given to Mr Metcalfe who was appointed Professor of Physics about eighteen months ago, except that Government would prefer his leave to be regulated by the Mysore Service Rules rather than by those of the Indian Institute of Science At the same time if you can get a better man who would make the leave rules of the Indian Institute of Science a sine qua non, you may kindly send in his application for consideration by Government I am sending you a copy of the Government Order appointing Mr Metcalfe and also a copy of the Mysore Service Regulations which may be shown to any likely candidate Under the new University Regulations the Summer Vacation will most likely last for about three months in the Central College

3 The Professor of Chemistry will be expected to teach and superintend the teaching of Chemistry for the B A Ordinary Course in Branches II A and II B of the Madras University He should be also qualified to teach Chemistry for the B A Degree with Honors in Branch II B I am sending you a copy of the Madras University Calendar which will give an idea of the standard

4 It is hoped that he will be able to join his appointment

at an early date in order to advise Government regarding the construction and equipment of the Chemical Laboratory

5 Mr Metcalfe is at present in England and can give any additional information to intending candidates His address is, 99, Belvedere Road, Upper Norwood, London, S E

I have the honor to be,

Sir,

Your most obedient servant,

(Sd) J Weir,

Inspector General

" True copy "

J Weir

Inspector General

Urgent

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OFFICE OF INSPECTOR GENERAL OF EDUCATION IN MYSORE

D 8635

No 11600/837 Encs 18

Bangalore 30 May 1910

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From

J Weir Esq , M A ,
~~H. J. BHABHA Esq, M.A~~

Inspector General of Education in Mysore

To

C S Balasurdaram Iyer Esq , B A ,
Offg Secretary to the Government of H H the Maharaja
of Mysore, General and Revenue Departments, Bangalore

SIR

In continuation of my letter No 11437 / 819 dated 9th May 1910 recommending Mr F L Usher as Professor of Chemistry, I have the honor to forward herewith the following papers received by this week's mail -

(1) Formal application from Mr Usher
(2) Testimonial from Professor Francis, Bristol University
(3) A statement of Mr Usher's Scholastic career and a list of his publications
(4) Copies of his publications (eight in number)

I have also the honor to inform you that Sir William Ramsay has forwarded an application from another candidate Dr David Thomson of Glasgow University The following papers are forwarded herewith -

(1) Formal application from Dr Thomson

(2) Letter From Dr Desch, Lecturer on Metallurgy, Glasgow University

(3) Copies of testimonials

(4) Copies of his publications (three in number)

(5) Official duplicate of Ph D diploma, Gottingen Universi

Mr Usher is 24 years of age and Dr Thomson is 31 but Sir William Ramsay considers that Mr Usher's work shows greater originality and recommends the selection of Mr Usher

I have the honor to be

Sir,

Your most obedient servant

J Wem

Inspector General

L B

University College,
London
May 10th, 1910

To the Inspector-General of
Education in Mysore

Sir,

I beg to offer myself as a candidate for the Chair of Chemistry in the Central College at Bangalore, I believe that Sir William Ramsay has already written to you suggesting my name

In support of my application I enclose a testimonial from Professor Francis, under whom I worked in the Laboratory of University College, Bristol, and I beg to refer you to Dr Morris W Travers, now Director of the Indian Institute of Science, with whom I worked at Bristol when he was Professor there I beg also to refer you to Sir William Ramsay, and to Professor Rothmund of Prague, in whose laboratories I have worked If required, I can ask several distinguished chemists who are acquainted with my work to furnish you with their opinion of it

I am 24 years of age and have always enjoyed good health Should you honour me by selecting me for the Chair of Chemistry, I should do my best to forward the interests of education in the Mysore State, and to infuse a spirit of research into my pupils

I enclose a tabular statement of my educational career, and a list of my publications

I remain, Sir,
Yours faithfully,

Francis L Usher

10
(2)

COPY

University of Bristol

Mr E L Usher was a student here between 1901-1907 and passed through his college career in the most satisfactory manner He has an excellent knowledge of Chemistry, and some years ago, on his own initiative carried out an admirable and now well-known investigation on the Photosynthesis of Chlorophyll

I have heard him lecture, he has a good style and treats a subject in a very clear and lucid fashion

During last summer 1909, he worked here in the vacation, and his manipulative skill was the admiration of the staff

I recommend him most heartily for the post for which he is applying and have no hesitation in saying that - if Mr Usher be appointed - he will be found a pleasant colleague and carry out his work to the satisfaction of his Principal and to the credit of the Institution

(Sd) FRANCIS FRANCIS
Professor of Chemistry

11
(3)

Educated at Weymouth College

Studied at University College, Bristol, 1901-7, under Professors Sydney Young, M W Travers, and F Francis

B Sc London, Honours in Chemistry, with Physics as subsidiary subject, 1906

Exhibition of 1851 Science Research Scholar, 1907-9

Worked in Institute of Physical Chemistry, German University, Prague, 1907-8

Worked in Chemical Laboratory, University College, London 1908 till present time

LIST OF PUBLICATIONS

(1) "On the Interaction of Sulphuretted Hydrogen and Arsenic pentoxide in presence of hydrochloric acid "
(Usher and Travers, Chem Soc Trans 1905 87 1370)

(2) "The Mechanism of Carbon Assimilation in Green Plants Part 1
(Usher & Priestley, Roy Soc Proc 1906 B 77 369)

(3) "The Mechanism of Carbon Assimilation in Green Plants Part 11 "
(Usher & Priestly, Roy Soc Proc 1906 B 78 310)

(4) 'On the behaviour of Certain Substances at their Critical Temperatures
(Travers & Usher, Roy Soc Proc 1906, A 78 247)

(5) "Über die Loslichkeit von NO in wasserigen Lösungen von $FeSO_4$ $NiSO_4$, $CoSO_4$, und $MnCl_2$"
(Usher, Zeit für physik, Chemie, 1908 62 622)

(6) "Uber die Einwirkung der Radium-Emanation auf die Elements der Kohlenstoffgruppe "

(Ramsay and Usher, Berichte 1909 42 2930)

(7) "The Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water "

(Usher, Chem Soc Trans 1910 97 66)

(8) The Influence of Radium Emanation on Equilibrium in the Gaseous System "

(Usher, Chem Soc Trans 1910 97 389)

THE INTERACTION OF SULPHURETTED HYDROGEN AND ARSENIC PENTOXIDE IN PRESENCE OF HYDROCHLORIC ACID

BY

FRANCIS LAWRY USHER

AND

MORRIS WILLIAM TRAVERS D Sc F R S

From the Transactions of th Chemi al S iety 1905 Vol 87

CXXXVII —*The Interaction of Sulphuretted Hydrogen and Arsenic Pentoxide in presence of Hydrochloric Acid*

By Francis Lawry Usher and Morris William Travers
D Sc F R S

The following invest gat on w s the out ome of some obse at ons on the separat on of arsenic from comme l hydrochlo c ac d by t e t ng t with sulphuretted hydrogen It was found as m ght have been expected that the arsen c p esent in the tervalent condition was mmediately and completely sep rated by the act on of the gas The arsen c present n the quinquevalent condition sep rated sl wly and appe red to be p ec p tated somet mes as a sen c penta lph de sometimes as the t isulph de m xed w th sulphu It appe red interesting to dete m ne unde what cond t ons each of these sub tances was formed and if poss ble to invest gate the mecha i m of the react on

Brauner and Tomíček (Trans 1888 53 145) who invest g ted the interact on of sulphuretted hyd ogen w th solut ons of arsen acid containing up to 8 pe cent of hydr chlor c ac d found that in absence of hydro hloric ac d a solution conta n ng 0 6 per cent of arsenic pentoxide gave a p ecip tate wh ch after emo ing the free sulphur consisted of 85 per cent of the pentasulph de In p es n e of 8 pe cent of hyd o hlor acid the prec p tate consi ted of the pure pentasulph de They d d not howeve ca y out any expe i ments with more concentrated acid

Experimental

We have epeated and confi med B auner and Tomíček s work in the case of solutions of dilute hydrochloric acid and have also

extended the investigation to solutions containing up to 32 cent of hydrogen chloride obtaining in the latter case different and interesting results which are given in the following table. The experiments were carried out at about 15 and in every case the solution contained 0 3664 per cent of the pentoxide

HCl per cent	Composition of precipitate	HCl per cent	Composition of precipitate
1 8	As_2S_5 91 per cent	14 34	As_2S_5 pure
7 9	As_2S_5 pure	25 10	As_2S_3 58 per cent
10 76	As_2S_5 pure	32 27	As_2S_3 pure

The solution was contained in a flask and sulphuretted hydrogen was slowly bubbled through the liquid at the rate of about five bubbles per second After about twelve hours the current of gas was stopped and the precipitate was collected washed with water and alcohol and extracted for six hours in a Soxhlet s apparatus with carbon disulphide the final product being analysed by the usual method

Study of the Reaction in presence of Small Concentrations of Hydrochloric Acid—The reaction between arsenic acid and sulphuretted hydrogen which results in the formation of arsenious sulphide and sulphur may be supposed to take place in two or more stages Thus

i $As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S$

ii $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$

The second reaction and possibly an intermediate reaction involving the formation of arsenic trichloride do not concern us as these reactions are certainly instantaneous

The reaction which results in the formation of the pentasulphide may be written simply

iii $As_2O_5 + 5H_2S = A\ _2S_5 + 5H_2O$

although it is probable that one is really dealing with a hydrated form of the pentoxide and that the equation does not strictly represent the fact

It was our object to investigate the conditions which favour reactions i and iii respectively but although it might have been possible to throw some light on the matter by studying the reaction velocity with different concentrations the experimental difficulties were considerable and on account of the complex character of the reacting substance we abandoned this idea

It appeared probable that the action of the hydrochloric acid was negatively catalytic either with regard to the oxidising action of the arsenic acid or to the reducing action of the sulphuretted hydrogen In accordance with this view we first of all studied the reduction and oxidation of these two substances respectively in presence of varying concentrations of hydrochloric acid

duction of a solution conta ning 0 684 per cent of arsen c by a solution of sulphur d oxide in p esence of va ying con rations of hydrochloric acid was first studied The results are as llows

As_2O p t.	SO p t.	HCl p t	R ult
( ) 0 684	3 272	4 9	C mpl t red t 45
(*b*) 0 684	3 272	20 3	28 3 p t. red d 45
( ) 0 684	3 272	32 0	C mpl t d t 45

The experiment *c* will be cons dered l ter With regard to *a* and *b* it s obvious that the rate of reduction of the pentoxide is cons derably retarded by the presen e of the hyd ochloric ac d

We next inve tigat d the rate of oxidation of sulphuretted hydrogen by iod ne and by ferric chloride in presence of va ying concent ations of hydrochlor c acid The sulphu etted hydrogen was in excess of the second reagent and the concentrations of the hydro hloric acid were 2 and 10 pe cent in the two samples The t me between the com mencement of the exper ment and the moment at wh ch the last t ace of iodine o fe ic s lt could be detected was obser ed The presence of the hydrochlo c acid appeared to have no effect on the velocity of the react on

It appears then that the effect of the p esence of the hydrochloric acid in the eact on between arsen c ac d and sulphuretted hydro en is due to ts nfl en e n the arsenic ac d It does not appear poss ble to give a mo e det led explanat n for although ar enic ac d s a fairly st ong acid and in d lute solution may be co s de ed as und rgo ng d ssoc at n the infl ence f the ncrease in concentra tion of the hyd ogen i ns du to the add tion of hydrochloric ac d in redu i g the concent at on of the arsen c conta ning ions throws no light on the me han sm of the re ct n

A few expe ment we e m de with solut ons conta n ng la ger quantit es of p ntox de It is unneces a y to ente into the details of these expe ments it suffi es to state that as might have been expected the tendency to fo m the t sulph de increased w th the concentr tion of the pentox de

Study f the React on in p esence of Concentrated H drochloric Ac d

It has been obs ed that the e ction of arsen c acid w th e ther phu etted hyd og n r sulphur dioxide in presence of concentrated drochlo ic acid results in its complete and rapid red ction to sen ous compounds

This react on probably finds an explanation in the fact that the ge may be represented by the equation

$$As_2O_5 + 10HCl \rightleftharpoons 2AsCl_3 + 2Cl_2 + 5H_2O$$

which is accompanied by further instantaneous reactions involving the formation of the trisulphide and sulphur from the sulphuretted hydrogen

It appears that the condition of equilibrium expressed by the foregoing equation shifts rapidly to the right with increasing concentration of the hydrochloric acid A small quantity of the dry pentoxide sealed up in a glass tube with pure anhydrous hydrogen chloride in the liquid state was rapidly acted on at the ordinary temperature After a few hours the white solid had disappeared and the tube contained two immiscible layers of liquid * On cooling the tube in liquid air breaking off the point and allowing the tube to regain the ordinary temperature hydrogen chloride and chlorine which formed the upper (yellow) layer were first given off the gas however did not contain arsenic The contents of the tube were then washed out and were found to contain a solution of an arsenious compound

UNIVERSITY COLLEGE
BRISTOL

When hydrogen chloride is condensed in a tube containing a small quantity of its saturated solution and the tube is sealed and allowed to warm up to the normal temperature two layers are formed the upper layer containing more hydrogen chloride than the lower On cooling to -18 the hydrate $HCl\ 2H_2O$ separates in equilibrium with pure liquid hydrogen chloride

[*From the* PROCEEDINGS OF THE ROYAL SOCIETY B VOL 77 1906]

A Study of the Mechanism of Carbon Assimilation in Green Plants

BY FRANCIS L USHER AND J H PRIESTLEY B Sc

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY B Vol 77]

A Study of the Mechanism of Carbon Assimilation in Green Plants

By FRANCIS L. USHER and J H PRIESTLEY B Sc Lecturer in Botany at University College Bristol

(Communicated by Professor M W Travers F R S Received December 16 1905 —Read January 18 1906)

(From the Chemical and Botanical Department of the University College Bristol)

Introduction —The investigation to be described in this paper has had for its object the elucidation of certain problems concerning the nature of the first stages in the assimilation of carbon from carbon dioxide by the green parts of plants and although far from complete it has been thought advisable to publish the results already obtained inasmuch as the weather is likely to hinder the experimental work for some time to come

In 1870 Baeyer put forward the hypothesis that formic aldehyde is the first product of the decomposition of carbon dioxide in the plant. This suggestion received some support from Bokorny * who proved in 1891 that starch was formed in the dark by the green filaments of *Spirogyra* when immersed in a solution of sodium oxymethyl sulphonate of 0 1 to 1 per cent strength

Bokorny s experiments are possibly open to the objection that formaldehyde condenses very readily to non poisonous carbohydrates in presence of sulphites or bisulphites and it has been shown by Laurent and Acton† that starch is formed in the dark from most sugars

Quite recently Bouilhac and Treboux‡ have succeeded in growing plants in a very dilute solution of pure formaldehyde Treboux has found that *Elodea* forms starch in the dark from a 0 001 per cent solution of formaldehyde and Bouilhac has shown that this is also the case with *Sinapis alba* and some *Algæ* Their experiments bring out in a striking manner the intensely poisonous nature of even very dilute solutions of formaldehyde

Evidence of this kind however is quite indirect and on this account greater importance attaches to the results obtained by Lach § who for the first time demonstrated the decomposition of carbon dioxide by light outside the plant He showed that by passing pure carbon dioxide through a 1 5 per cent

* B ht 1891 ol 24 p 103
† Roy S c P oc 1890 l 47 p 150
‡ Bl 1903 p 3
§ C R l 1893 l 116 p 114

olution of uranium acetate exposed to sunlight in a glass apparatus a precipitate consisting of a mixture of uranium peroxide with lower oxides was formed and that the solution contained formaldehyde Bach regarded the uranium acetate solution as playing the part of a chemical and an optical sensitiser and considered the decomposition of the carbon dioxide to result primarily in the production of hydrogen peroxide and formaldehyde

Decomposition of Carbon Dioxide Outside the Plant—The experiments of Bach have been repeated and confirmed both as to the production of peroxide and formaldehyde

The amount of decomposition obtained in three weeks in bright weather was extremely small and this appears to us to be explained by the fact that (1) as a chemical sensitiser uranium acetate is far inferior to that which exists in a green plant inasmuch as the separated oxygen (in whatever form it may exist) is not entirely removed from the sphere of action as in the case of the plant but remains as a fairly insoluble peroxide which undergoes a reversible change with the other product namely formaldehyde (2) as an optical sensitiser uranium acetate is inferior to chlorophyll to the extent that it possesses no absorption at all in the red and only two faint bands between F and G

In view of the extreme slowness of the reaction under these conditions experiments were made with very large concentrations of carbon dioxide Tubes of Jena glass 40 cm long and 8 to 10 mm bore were about three quarters filled with 1 5 per cent uranium acetate solution and cooled in liquid air while some carbon dioxide was passed in They were then sealed and suspended outside a south window in bright sunshine Within 15 minutes of warming up to the air temperature a precipitate began to form and in 24 hours the reaction was complete The tubes when opened were found to contain uranium peroxide and formic acid but no formaldehyde The formic acid was obtained by distillation of the filtrate from the peroxide and was characterised by (1) reduction of silver nitrate (2) reduction of Fehling's solution and (3) properties of lead salt

Thus with very large concentrations of carbon dioxide formic acid and not formaldehyde results

These experiments are open to the objection that since uranium acetate is to a considerable extent hydrolysed in solution the formaldehyde in one case and the formic acid in the other may possibly have been derived from the acetic acid present

It has been found that uranium sulphate in a 2 per cent solution functions in the same way as the acetate An experiment with the sulphate conducted in the usual way *i e* bubbling carbon dioxide through the solution which

lasted over three weeks in very dull weather gave uranium peroxide and formic acid The different results obtained here from those in the case of similar experiments with the acetate may be due to the reduction potential falling below the limit required for the completion of the second stage of the decomposition

In all the foregoing experiments except in the case of the liquid carbon dioxide tubes blank experiments were simultaneously performed (1) with uranium solution and carbon dioxide in the dark and (2) with carbon dioxide free solution in the light In neither case was any precipitate formed

Decomposition of Carbon Dioxide in the Plant—If a similar reaction resulting in the formation of formaldehyde and a peroxide takes place in the first stage of the absorption of carbon dioxide by the plant it is obvious that both the initial products of decomposition must undergo a rapid change

On account of its intensely poisonous nature formaldehyde must be very rapidly converted into some physiologically inert substance and the peroxide must be decomposed with evolution of gaseous oxygen a process which follows exposure to light by an interval of one or two seconds

The problem then is to ascertain the process by which oxygen is disengaged to show the actual presence of formaldehyde localised in the neighbourhood of the chloroplast and to trace the steps by which the formaldehyde is polymerised

The Mechanism of the Evolution of Oxygen from the Green Plant—In the experiments relating to the decomposition of carbon dioxide outside the plant no evolution of oxygen gas is ever observed it remains in the system as a peroxide

There have been conflicting statements with regard to the presence of hydrogen peroxide in plants but even if traces are to be found there is no evidence that it is a product of decomposition of carbon dioxide It has indeed been shown that several organic substances notably the organic acids *eg* oxalic give rise to hydrogen peroxide on exposure to light and such substances as these are of common occurrence in the leaves of plants If however hydrogen peroxide is one of the first products of the photolysis of carbon dioxide we are more directly concerned with the elimination of oxygen in the gaseous form than with the detection of the peroxide

Hitherto those writers who have recognised the difficulty at all have suggested some method of reduction which of course leads back to the starting point It appeared much more probable that this step in the process was brought about by a catalyst probably an enzyme To test this sug *Elodea* was immersed in a dilute solution of hydrogen peroxide An

immediate and rapid decomposition set in and a gas was freely evolved which was found to be oxygen The action proceeded as rapidly in the dark as in the light

The following experiments were performed with the object of ascertaining the nature of the catalyst —

(*a*) A plant was immersed in boiling water for 30 seconds and was subsequently found to be without action on hydrogen peroxide

(*b*) After treatment with dilute solutions of iodine mercuric chloride and hydrogen sulphide no action took place

(*c*) Some *Elodea* was suspended in air charged with chloroform vapour for two hours in order to kill the protoplasm and was then allowed to recover for a similar period Rapid disengagement of oxygen took place

(*d*) After immersion in very dilute formaldehyde solution hydrogen peroxide was not decomposed

These experiments seem to point to the existence of a catalysing enzyme Several attempts to extract it by simple maceration with water or salt solution failed and we were also unable to extract it after powdering leaves in liquid air Following a suggestion of Dr Horace Brown we ultimately succeeded in obtaining it by previously drying a quantity of *Elodea* and subsequently digesting with water at 30° for 48 hours The enzyme was precipitated by an excess of absolute alcohol and dried

By this process it is obtained as a light brown powder containing diastase whose aqueous solution energetically decomposes hydrogen peroxide whereas ordinary malt diastase does not Whether the enzyme is one already known or whether it is secreted specially for the purpose of catalysing hydrogen peroxide we cannot as yet say

On mounting a leaf of *Elodea* in very dilute hydrogen peroxide and examining microscopically under a high power bubbles of gas were seen to emerge from the chloroplasts only an observation which shows the strict localization of this enzyme to the seat of the photosynthetic process

In regard to the distribution of this enzyme we have examined the foliage leaves of plants belonging to 46 Natural Orders and representative of the Vascular Cryptogams and all the main groups of the Phanerogams and have found the power of catalysing hydrogen peroxide in every case though the energy of the decomposition varies considerably in different groups It also occurs in etiolated leaves and in potato tubers and in fact appears to be associated with amyloplasts whether possessing chlorophyll or not

The Production of Formaldehyde and the Manner of its Removal—It has been found in the case of *Spirogyra* that starch appears in a previously

starches filament within three minutes of exposure to light and it is probable that some sort of carbohydrate is formed much sooner than this or it has been shown by Brown and Morris* that starch is probably not elaborated within the cell until the supply of nutriment is in excess of the cell requirements

It would therefore seem as though the arrangement which exists in the plant for the removal of formaldehyde is at least as efficient as any external arrangement we can make to remove it in a different way without at the same time killing the plant and thus eliminating one of the essential factors namely the vitality of the protoplasm

For this reason it is useless to look for formaldehyde in healthy assimilating leaves It is well known that certain chemical substances possess the property of condensing formaldehyde to various carbohydrates chiefly formose acrose and methylenitan It has been found by Loew† that such condensing agents are chiefly metallic oxides and acid sulphites substances not likely to occur in plants

Moreover condensation by these bodies is a comparatively slow process and quite inefficient when applied to the requirements of a plant Nevertheless if the condensation in the plant were due to some chemical agent stored in the neighbourhood of the chloroplast it should still be capable of taking place when the protoplasm of the leaf is killed and its enzymes destroyed

Some healthy green sprigs of *Elodea* were immersed in boiling water for 0 seconds in order to kill the protoplasm and destroy the enzymes They were then placed in water saturated with carbon dioxide and exposed to sunlight In the course of a few hours the deep green colour of the leaves had been completely bleached and on immersing the bleached sprigs in a solution of rosaniline decoloured with sulphurous acid a red colour was developed

The original green material when treated in this way exhibited no colouration There was therefore some substance of an aldehydic nature present in the killed and bleached leaves which was absent in those which were alive The sequence of events in this experiment may be described as follows —Photolysis of carbon dioxide begins in the normal way giving rise to hydrogen peroxide and formaldehyde The enzymes having been destroyed the hydrogen peroxide instead of being catalysed in the usual manner oxidises the chlorophyll to a colourless substance at which point the reaction necessarily comes to an end Meanwhile a quantity of

* J C S 1893 T p 632
† B lt 1888 p 2 1

formaldehyde equivalent to the hydrogen peroxide required to destroy the chlorophyll accumulates and thenceforward the reaction is strictly reversible

The following experiments were performed to settle the points involved in this explanation —It was in the first place necessary to show whether the colouration referred to above was due to formaldehyde For this purpose some leaves killed and bleached in carbon dioxide solution as described were soaked for 12 hours in aniline water and were then examined microscopically under a high power Some leaves which had been killed and simply decolourised with hydrogen peroxide were treated in the same way

In the first case the decolourised chloroplasts were observed to be the centres of clusters of well defined crystals identical in appearance with those of methylene aniline artificially prepared from aniline water and formaldehyde They were soluble in dilute mineral acids and also in warm alcohol from which they crystallised in the cell on cooling The leaves artificially decolourised with hydrogen peroxide showed no crystals

An attempt was then made to obtain the formaldehyde outside the plant For this purpose a large quantity of *Ulva* and *Enteromorpha* was killed and bleached in carbon dioxide solution and subjected to steam distillation The distillate was divided into two parts To the larger of these was added some aniline water

A white precipitate was formed after some time which was collected and heated side by side with a comparison tube containing methylene aniline It melted not quite sharply three or four degrees below the pure artificially prepared substance The other portion of the distillate was evaporated with ammonia on the water bath and the residue dissolved in water and treated with bromine water gave the characteristic tetra brom derivative of hexamethylene tetramine

Hence leaves in which both protoplasm and enzymes have been killed when placed under conditions favourable for assimilation develop formaldehyde until the photolytic process is brought to an end by the destruction of the chlorophyll

It was next necessary to determine whether the condensation of the formaldehyde is due to an enzyme secreted by the chloroplast or whether the protoplasm of the granule itself effected it Some *Elodea* was suspended in air charged with chloroform vapour for two hours by which means the protoplasm was killed without affecting the enzymes It was then exposed to sunlight in saturated carbon dioxide solution In a few hours the chlorophyll became bleached and formaldehyde was subsequently found in the plant

It follows from this that the protoplasm of the chloroplast is the condensing agent The bleaching of the chlorophyll in this case is due to the fact that the enzyme though unharmed at the commencement of the experiment quickly becomes poisoned by the accumulating formaldehyde In this last experiment the limit to the accumulation of formaldehyde in a plant is realised since there is formed an amount equivalent to that amount of hydrogen peroxide which is catalysed before the enzyme ceases to act together with an amount equivalent to the hydrogen peroxide required to destroy the chlorophyll

That a certain amount of hydrogen peroxide is catalysed when the protoplasm only is dead was shown in the following manner Approximately equal quantities of *Elodea* were taken one of which (A) was killed by immersion in boiling water another (B) was suspended for two hours in air saturated with chloroform vapour to kill the protoplasm and not the enzymes while the third (C) served as a control

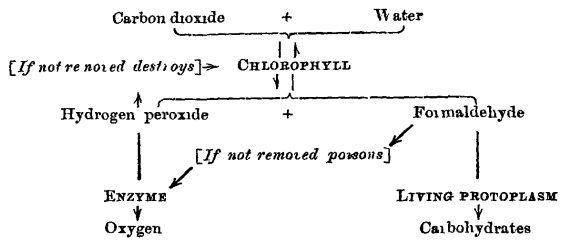
All three were placed in carbon dioxide solution under funnels with inverted test tubes and exposed to artificial light for 12 hours From A there was no evolution of oxygen from B 0 3 c c were given off and from C 2 8 c c In the case of P after exposure to light no catalytic action on hydrogen peroxide could be observed while previously vigorous decomposition had taken place

Summary

1 The photolysis of carbon dioxide may take place outside the plant in absence of chlorophyll provided one of the products is removed
2 The normal products of the photolysis are hydrogen peroxide and formaldehyde though under certain conditions formic acid may be formed
3 In the plant the decomposition of the hydrogen peroxide is provided for by a catalysing enzyme of general occurrence
4 The condensation of the formaldehyde is dependent on the healthy condition of the protoplasm

There are therefore three factors essential to photosynthesis from carbon dioxide and water in the plant they are (i) vitality of the protoplasm (ii) presence of a catalysing enzyme and (iii) presence of chlorophyll If any one of these factors be interfered with the process of photosynthesis ultimately comes to an end through the destruction of the optical sensitiser chlorophyll

The relations between the various factors in this process may be diagrammatically expressed thus —



In conclusion we wish to express our indebtedness to Dr Travers and to Dr Horace Brown for their valuable suggestions and help in the course of this research

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[*From the* PROCEEDINGS OF THE ROYAL SOCIETY A VOL 78 1906]

On the Behaviour of Certain Substances at their Critical Temperatures

BY MORRIS W TRAVERS D Sc F R S AND FRANCIS L USHER

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY A Vol 78]

On the Behaviour of Certain Substances at their Critical Temperatures

By MORRIS W TRAVERS D Sc F R.S and FRANCIS L USHER

(Received June 13 —Read June 21 1906)

A work entitled Le Point Critique des Corps Purs has recently been published by E Mathias whose opinion on matters relating to the critical state must always carry weight In this he discusses at length the various theories which have been put forward to explain certain irregularities observed in the behaviour of substances which were supposed to be pure at their critical temperatures These irregularities are not accounted for by the simpler theories of Andrews and Van der Waals He calls attention to the experiments of certain investigators which appear to suggest that the currently accepted values of the critical constants of many common substances may be vitiated either owing to the time allowed for the establishment of equilibrium between the coexisting phases near the critical point being insufficient or the temperature at which the dividing surface vanishes not being independent of the relative masses of the two phases at the temperature at which this takes place

According to I Traube substances contain different kinds of aggregates which he calls gasogenic and liquidogenic molecules It follows that if equilibrium demands that there shall be a certain concentration of these molecules in the vapour and liquid phases respectively then unless dissociation and association take place instantaneously there must elapse a time following any change of condition before equilibrium can be established between the two phases

P de Heen s theory goes further and assuming the existence of such complexes suggests that it is possible that the concentration of them in the two phases is a function not only of the temperature but also of the relative masses of the two phases or in other words of the mean specific volume of the system under investigation In this case a system

apparently consisting of a simple substance may be to take the simplest case bivariant instead of being univariant as is usually assumed

This last theory may of course represent a condition either of true or false equilibrium and in support of the latter supposition certain indirect evidence is forthcoming Brereton Baker has shown that association and dissociation are delayed and accelerated by the presence of minute traces of certain foreign substances The dissociation of mercurous chloride Hg_2Cl_2 into 2HgCl takes place so slowly in the absence of water vapour that the vapour density of the dry substance is almost exactly twice that of the chloride which has not been so thoroughly dried It follows that two such samples of mercurous chloride would at the same temperature have different vapour pressures and that if dissociation took place very slowly the intermediate mixtures which would be formed would constitute bivariant systems

The case in which the velocity of dissociation approaches zero corresponds to that involved in de Heen s theory Traube s view really involves no new principle Whether however the views of either of them can be realised experimentally is the question which we have now to consider

The conclusions which have been drawn from the experimental work on which these theories are based have given rise to a distinction between the temperature at which the surface separating the two phases disappears which is referred to as the temperature of Cagniard Latour and that at which the densities of the substance in those parts of the tube formerly occupied by the two phases become equal which as in the case of mixtures is called the critical temperature That the former is a function of the relative masses of the coexisting phases at the moment of the disappearance of the surface is the first consequence of de Heen s theory and that the results are markedly influenced by a time factor would follow from Traube s theory We find however that the results of our own experiments in no sense confirm this conclusion and in fact support the views of S Young and others who are opposed to it We have not investigated the second consequence of the theory that the densities of the two phases do not become identical at the Cagniard Latour temperature However it appears more than probable that if the first consequence falls to the ground the second will follow it amongst a considerable amount of experimental evidence in opposition to it perhaps nothing is more convincing in this respect than Ramsay s simple demonstration of the equality of the densities of the two phases at the temperature of Cagniard Latour *

It is worth while quoting some of the experimental results on which

* Zeit Phys Chem ' vol 14 p 486

de Heen's and Traube's views are based. The results of Ratelli, Ambrosi, Galitzine and others are given in Mathias' book, but those of the first named will serve as an example. They are as follows —

Substance	Date	Mean specific gravity of the substance	Mean critical temperature
Alcohol	1891	0·3195	236·59
		0·3448	237·26
		0·3888	235·94
		0·3893	235·67
	189	0·3439	237·0
		0·4000	236·43
Eth	1891	0·2409	193·60
		0·2767	193·44
		0·2889	193·17
		0·3043	193·01
	1892	0·2[illegible]0	192·63
		0·3192	192·12

It cannot fail to be noticed that these results do not even show an agreement among themselves. It is common knowledge that it is very difficult to obtain pure dry alcohol and that only prolonged washing with water will remove the last traces of alcohol from ether. Our first experiments with ether which had only been washed a few times with water led to results similar to those obtained by Ratelli.

There is however another interesting phenomenon which has been observed in connection with those which take place at the critical temperature. It appears that Altschul was the first to observe that in the case of most liquids there appeared at the critical temperature (Cagniard Latour) at the level in the tube at which the surface vanished an opalescent band. His description of the effect is somewhat obscure and neither from him nor from Wesendonck† have we been able to derive a complete idea of what happens.

As this particular phenomenon appeared to call for further investigation and as in spite of much evidence to the contrary there appeared to exist a doubt as to whether the simple theories of Andrews and Van der Waals were sufficient to account for the changes which take place at the critical temperature, we decided to undertake the experiments which are described in the latter part of this paper. It suffices to state in advance that in making the observations we employed comparatively large masses of the liquids enclosed in thin walled glass tubes and that particular precautions were taken

* Z. f. Phys. Chem., vol. 11, No. 189, p. 578.
† Zeit. Phys. Chem., vol. 15, p. 262.

to obtain them pure and to introduce them into the experimental tubes without contamination Further arrangements were made for maintaining a very steady temperature which could be allowed to rise very slowly towards the critical point

The Phenomena which Accompany Disappearance of the Surface at the Critical Temperature

It must be observed in the first instance that the following phenomena take place at a temperature or are distributed in the same invariable order over a range of temperature which is dependent only on the nature of the substance under investigation and that they appear to be absolutely independent of the relative masses of the coexisting phases That is to say if we consider any part of the process such as the disappearance of the dividing surface we find that so long as the mass of liquid in the tube falls within certain limits it takes place at a temperature which is constant within the limit of accuracy of the experiments and in our own experiments to within 0° 05

If we heat in a glass tube varying masses of a pure liquid we observe as we approach the temperature at which the surface of separation vanishes one or other of the following changes taking place —

(*a*) The liquid will have completely evaporated before the true critical temperature is reached and in this case there is insufficient liquid in the tube

(*b*) The surface will sink towards the bottom of the tube and at the critical temperature will disappear at a short distance above it

(*c*) The surface will neither rise nor fall while the tube is heated through the last small temperature interval and at the critical temperature will disappear about the middle of the tube

(*d*) The surface will rise and at the critical temperature will vanish near the top of the tube

(*e*) The liquid will fill the tube before the true critical temperature is reached and if the temperature is raised the tube will probably burst, in this case there is too much liquid in the tube

If the conditions described under headings (*b*) (*c*) and (*d*) are produced in tubes of sufficiently large diameter (in the case of our experiments about 1 cm in diameter and 20 cm long) the temperature being allowed to rise so slowly that the two phases are brought into equilibrium without ebullition of the liquid phase the following phenomena will be observed —

In case (*b*) at a temperature slightly below that at which the surface vanishes the space below the latter will become opalescent appearing brown by transmitted light and whitish by reflected light. The effect is not

altogether dissimilar to that produced by the action of an oxidising agent on a solution of sulphuretted hydrogen The nearer the surface is to the bottom of the tube the more intense is the opalescence So long as the surface is still visible the effect is limited to the space below it and though it is fairly evenly distributed throughout that space it is usually slightly more intense just below the surface When the surface vanishes the upper limit to the effect becomes less clearly defined and if sufficient time is allowed it becomes diffused throughout the whole tube the same result may be arrived at by stirring the contents of the tube by means of an iron stirrer operated by a magnet outside the tube

When the surface disappears there is observed in the case of sulphur dioxide evidence of optical discontinuity between the substance in the tube above and below the point at which this takes place it appears however to be merely transient in character and if it does not vanish without the temperature being raised it is certainly incapable of existence at a temperature 0 05 above that of the disappearance of the surface. The opalescence appears to persist over a finite range of temperature it rises in in the case of sulphur dioxide at 0 1 below that at which the surface vanishes attains a maximum at about 0 05 above it and has completely disappeared at a temperature 0 1 higher In the case of ether the effects persist over about 2

Under the conditions included under heading (*d*) the position in the tube at which these phenomena make their appearance is exactly reversed The opalescence *appears above the surface* and its intensity increases as the latter disappears on approaching the top of the tube

If while the tube is being heated through the last small temperature interval below the temperature at which the surface vanishes the latter remains stationary the tube at the same time appears slightly and evenly opalescent throughout its whole length This corresponds to condition (*c*) As we have already stated the same effect can be produced by stirring the contents of the tube at any moment when the opalescence is observed above or below the surface itself or the point at which it has vanished

Conditions (*b*) and (*d*) can be reproduced in the following manner If when the condition corresponds to (*c*) and the temperature is within the range over which the opalescence is visible the volume of the space containing the substance is increased or decreased so slowly that the temperature is not lowered or raised appreciably opalescence will appear below or above the surface itself or the point at which it vanished and its intensity will be proportional to the space it occupies

In the case of some experiments which fall under headings (*b*) or (*d*) it

was observed that when the opalescence first made its appearance it was most intense immediately below or above the surface This effect was only transitory in character and it appeared as if the material giving rise to it were rapidly distributed by convection or diffusion throughout the phase in which it was formed

Discussion of these Results

In the first place our experiments appear to indicate that liquid vapour (one component) systems in the neighbourhood of the critical point are univariant as the simple theory demands If complex molecules of different magnitude exist equilibrium must be so rapidly established between them and the simple molecules as to negative de Heen s theory and to render Traube s theory unnecessary We now pass on to consider the phenomenon of opalescence

The observations of Altschul and Wesendonck* only extended to the formation of an opalescent band at the point at which the surface between the liquid and vapour vanished at the critical point and their descriptions convey the impression that the phenomenon is much simpler than appears from our experiments Bakker s explanation of the effect † which he attributes to the thickening of the surface layer as the temperature approaches the critical is based on their work

It may be pointed out that in tubes of small bore the transient effect which was described in the last paragraph of the previous section of this paper may appear to have a prominent character as an opalescent band replacing the dividing surface

On considering the facts before us we were drawn to the conclusion that there might be a certain resemblance between the systems we were dealing with and those which constitute colloidal or so called pseudo solutions The existence of molecular complexes did not appear to be a tenable hypothesis for reasons which have already been stated, but the optical effects appeared to point to the presence of non molecular aggregates Before we proceed further however it will be well to consider certain views as to the constitution of colloidal solutions which have been put forward by Donnan ‡ and a suggestion of his with regard to the application of the same theory to the explanation of the appearance of opalescence at the critical temperature

In dealing with colloidal solutions he combats the view that their

* *Loc cit*
† Zeit Phys Chem vol 49 p 609
‡ Zeit Phys Chem, vol 46 p 197

properties are in any way connected with the existence of very large molecules and considers the conditions under which one phase of a system would be distributed throughout the other in a state of very fine division as constituting a different phase So far he is of course dealing with two component systems though the nature of the aggregates is not altogether different from those which we shall refer to directly

At the British Association in 1904 Donnan put forward a suggestion for discussion as to the conditions which were necessary for the existence of such complexes in a liquid vapour one component system in the neighbourhood of the critical point He suggests that at the critical temperature the interfacial tension becomes zero for ordinary values of the radius of curvature but remains positive for very small values for which it does not become zero till the critical temperature is passed Hence we may assume that at temperatures slightly below the critical the interfacial tension is greater for very small radii of curvature than for ordinary curvatures

Over a range of temperature including the critical temperature limited above by the temperature at which the interfacial tension for small radii of curvature becomes zero and below less sharply we can imagine that small non molecular aggregates or drops can be differentiated from either the liquid or vapour phase and have a stable existence To such aggregates can we attribute the phenomenon of opalescence and the range of temperature over which it is observed and the manner of its appearance and disappearance are in agreement with the assumptions

The manner in which such aggregates or drops could be formed lies outside the discussion but it is possible to arrive at an explanation of the fact that the opalescence is confined to the phase which is decreasing in volume through movement of the dividing surface or at least is more intense in that phase Since it is an essential character of the aggregates that they are non molecular one cannot imagine them passing from the liquid to the vapour phase by the ordinary process of evaporation forming for a moment a constituent of the surface layer Further the existence of the aggregates assumes that the interfacial tension at their surfaces is greater than that at the surface dividing the liquid and vapour in the tube of which the radius of curvature is very large Hence an aggregate in contact with the surface will not coalesce with it as would a small drop with a larger surface under ordinary conditions The result would be that supposing that a certain number of aggregates were formed in either phase they would remain in that phase so long as they had a concrete existence and the optical effect to which they would give rise would depend on their dimensions and the number of them in a given space

Experimental Arrangements

Method of Maintaining Constant Temperatures—The apparatus employed was a modification of that described by Ramsay and Young * The experimental tube was enclosed within a vapour jacket which was surrounded by two outer tubes on one of which a scale was ruled The top of the jacket was connected with a large air reservoir and a manometer by means of which the pressure could be measured

In the experiments with sulphur dioxide the temperatures were determined by reading the pressures and referring to Ramsay and Young s table of vapour pressures but as this does not extend to pressures above 800 mm we determined the temperatures corresponding to the higher pressures by means of a Callendar platinum thermometer for which the constants have already been published † To avoid possible confusion in the future we set down the following data —

Vapour pressure of aniline	Temperature from platinum thermometer
772 7	185°
793 4	186
814 8	187
835 9	188
857 6	189
879 8	190
902 0	191
925 0	192
949 0	193
972 9	194

It is interesting to note that though by using aniline we were able to maintain and to recover temperatures constant to nearly 1/50° C we were quite unable to obtain such good results by employing quinoline which boiling under a pressure of about 260 mm gives a temperature corresponding to that of aniline boiling under a pressure of 960 mm This is probably due to the fact that the pressure of the vapour in the apparatus is the sum of the vapour pressures of quinoline and of mercury the latter being used to cover the rubber stopper which closes the opening at the bottom of the vapour jacket and that the saturation of the space inside the apparatus with mercury vapour is not complete The consequent variations in the temperature will be a function not only of the total saturation pressure of the

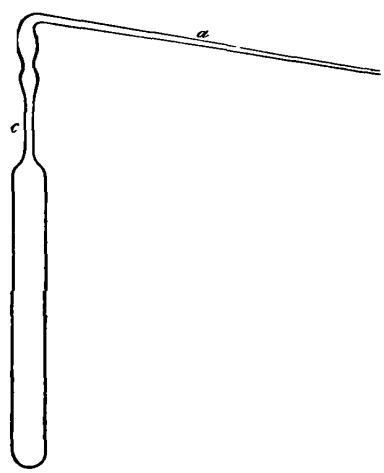
* Chem Soc Journ 1885 vol 47 p 640
† Roy Soc Proc 1905 vol 74 p 528

mercury vapour at the temperature of the experiment but also of its relative partial pressure in the mixture

To guard against accident through the bursting of one of the experimental tubes the apparatus was enclosed in a cubical box of about one metre on the edge open at the back and with an opening covered by a glass plate 2 cm thick in front On the two or three occasions on which the experimental tube burst though the vapour jacket and guard tubes were shattered no other damage was done.

Experiments with Ether

Preparation of Pure Ether and Method of Filling the Experimental Tubes — The ether was prepared from pure alcohol by the continuous process About 1½ litres of the liquid was washed with caustic soda solution and was then shaken 25 time with about its own volume of fresh ater to remove alcohol I ather less than ½ litre of liquid remained this was allowed to stand for a week in a bottle with excess of calcium chloride and (after shaking with dilute sodium amalgam to remove traces of ethyl peroxide) was transferred to a flask containing a large quantity of fine potassium wire After a week the liquid was distilled and though only the middle fraction was collected the whole mass appeared to evaporate at a temperature which was constant to within 0 02 to 0 03



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The experimental tubes which were of Jena hard glass were 20 cm long 0 8 cm internal diameter and 1 mm thick in the walls and were made in the form shown in fig 1 They were first partially filled with ether by dipping the capillary *a* into the ether and alternately warming and cooling The tube was then cut off at *b* the lower end was then cooled in liquid air while the open end was connected by a rubber tube with a Topler pump The tube was then completely exhausted and the exhaustion was continued while the solid melted When the ether was evaporating freely into the pump the tube was sealed at *c* in a blow pipe flame

Details of Experiments with Ether—Three tubes were used in these experiments The mean specific volume that is to say the volume of the tube divided by the mass of ether contained in it is given below the three tubes being referred to by the letters A B and C —

	c c per gramme		c c per gramme		c c per gramme
A	4 10	B	3 96	C	3 56

At the normal temperature the fraction of the total volume which the liquid occupied was in the three tubes respectively —

	c c per gramme		c c per gramme		c c per gramme
A	0 35	B	0 37	C	0 41

The following are the details of the experiments —

Tube and date	Pressure of aniline vapour	Temperature from platinum thermometer	Remarks
	mm		
A 21/3	962 5	193 57	Temperature falling from above T mist appeared and then liquid which filled one fourth of tube whole tube opalescent Tube cooled and re heated
	963 3	193 60	Temperature rising slowly Meniscus falling Whole tube very opalescent *liquid more so than vapour* As the meniscus fell the region *just above it* remained more strongly opalescent than the remainder of the tube Tube cooled and re heated
	963 4	193 60	Meniscus becoming nebulous and replaced by opalescent band Point of disappearance less than one fourth from bottom of tube
	964 3	193 64	Meniscus quite gone opalescence very marked but diffused at point of disappearance Ultimately opalescence diffused throughout tube Opalescence persisted for at least two degrees above Tc
A 22 3	963 4	193 70	At this temperature the meniscus completely vanished as at 193° 64 on the day before The behaviour of the ether in the two experiments was identical
B 22/3	963 0	193 59	Meniscus falling very slightly liquid occupying about two fifths of tube
	963 1	193 59	Meniscus still slowly falling In this experiment the effects observed were similar to but less marked than in the case of A
	963 2	193 60	Meniscus becoming nebulous and finally disappearing slightly below two fifths from bottom of tube The whole tube was then opalescent particularly at point of disappearance of meniscus
C 22/3	963 3	193 60	Liquid filling about five sixths of tube *vapour much more opalescent than liquid* Meniscus rising and leaving opalescent band behind it
	963 6	193 62	Meniscus very close to top of tube becoming nebulous and disappearing leaving the whole tube opalescent

13-20

Experiments with Sulphur Dioxide

Source of the Sulphur Dioxide and Method of Filling the Experimental Tubes—The substance was obtained in the first instance from a syphon of the commercial liquid Part of the liquid was allowed to evaporate from the syphon and then a quantity of it amounting to about 70 c c was introduced into the bulb *a* (fig 2) which contained excess of phosphorous pentoxide and which was cooled in a freezing mixture The stem was then sealed at *l* the bulb was removed from the mixture and about a quarter of the liquid in it was allowed to evaporate so as to remove all traces of air from the apparatus

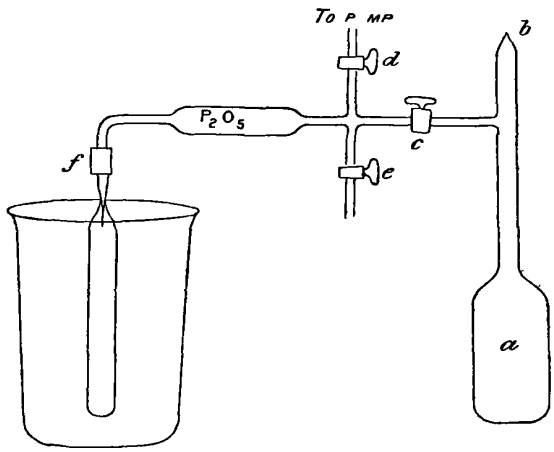

Fig 2

The experimental tube was attached by means of rubber pressure tubing at *f* When it was in position the whole of the apparatus on the left hand side of the stop cock *c* could be exhausted through the stop cock *d* which was closed while the apparatus was washed out with sulphur dioxide and finally filled During the latter operation the experimental tube was cooled in a freezing mixture more sulphur dioxide was introduced than it was intended that the tube should eventually contain the excess being allowed to evaporate into the pump or to escape into the air through the stop cock *e* The tube was finally sealed at the constriction while the pressure in it was still below that of the atmosphere

It will be observed that we have no direct guarantee of the purity of the

sulphur dioxide But the results of our experiments on the critical behaviour of successive fractions of the same quantity of liquid indicate that they are at least identical in their properties and with almost equal certainty that they all consist of one and the same simple substance

Preliminary Experiments with Sulphur Dioxide—In the first set of experiments which we wish to record we employed two sealed tubes about 14 cm long (not counting the length of the capillary portion) and 1 cm in diameter The mean specific volumes of the substance in the two tubes referred to as A and B were as follows —

	c c per gramme		c c per gramme
A	1 75	B	1 67

The tubes were heated as in the case of the experiments with ether in the vapour of aniline and as the temperatures were deduced by interpolation from the results of Ramsay and Young s experiments it is not necessary to set down the corresponding pressures In the following experiments the two tubes were heated together in the same vapour jacket —

Temperature	Remarks on A	Remarks on B
18	Liquid occupies 0 34 total volume	Liquid occupies 0 40 total volume
156 °5	0 07	0 90
	As the temperature was raised the liquid in A and the vapour in B becam opalescent the surface in the former rising and in the latter falling It was noticed that though the temperature could be maintained very constant at any point equilibrium was only slowly established some minutes elapsing before the meniscus came to rest and the maximum opalescence was attained	
157 *5*	At this temperature the surface in each tube became indistinct finally disappearing after some minutes the opalescence vanished	

Second Series of Experiments with Sulphur Dioxide—In these experiments arrangements were made for changing the volume of the substance under investigation by means of a compression apparatus for stirring it by means of a magnetic arrangement during the experiment and for measuring the temperature of the interior of the tube as well as of the jacket by means of a thermo electric junction

The apparatus is shown in section in fig 3 Into a steel cylinder *b* was screwed a steel tube *a* about 150 cm long connected with another horizontal cylinder into which a piston could be forced by means of a screw so as to decrease the internal volume of the apparatus which contained mercury The experimental tube which was about 1 cm in diameter and 50 cm long was cemented into the plug *c* which was screwed into *b* the

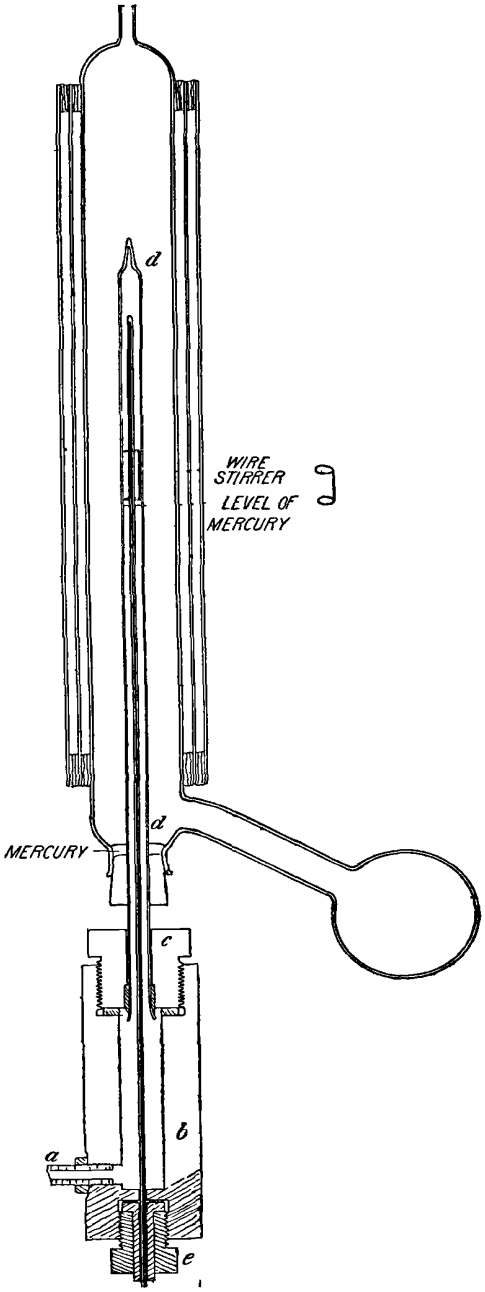

FIG 3

Thermo ele t c j n t ns at top and at l v l of t e At b ttom of fig e fo r w e should ha e been shown

junction being made good by means of a leather washer The thermo electric junctions were enclosed inside a capillary tube of very thin Jena hard glass which was cemented into a screwed plug *e* and was so arranged that one junction was at the top of the experimental tube close to the constriction and another which was enclosed within the same tube terminated about 5 cm lower down The stirrer consisted of a piece of soft iron wire bent so as to form two circles a little smaller than the inner diameter of the tube joined by a straight piece about 2 cm long at right angles to them The stirrer was operated by means of a powerful electro magnet the poles of which lay close to the outer guard tube of the vapour jacket

The following is a summary of several independent sets of experiments The measurements of the mean specific volumes of the substance in the experimental tube are only approximate —

Temperature at which surface vanished	Mean specific volume of substance	Remarks
?	2 3	Probably too little liquid in tube
157 24	2 1	(*a*) When stirred surface vanished at bottom of tube No opalescence (*b*) When not stirred optical discontinuity at 12 mm from bottom No opalescence
?	2 05	Surface disappeared at bottom of tube
157 22	2 0	Opalescence at surface 15 mm from bottom of tube On stirring opalescence was distributed throughout range through which stirrer moved and optical discontinuity appeared at upper limit of stirring
?	1 9	As before
?	1 8	Volume was *reduced* while the temperature was 157 2 opalescence became very marked particularly above surface and diminishing in intensity towards top of tube Temperature rose to 157 26 on stirring optical discontinuity moved to upper limit of stirring and opalescence distributed itself over the same range
157 2	1 9	Volume was *increased* while the temperature was 157 2 when opalescence appeared in liquid spreading downwards from surface Maintaining the temperature steady at 157 2 and the volume constant the opalescence gradually diffused throughout the tube after 20 minutes it was impossible to see the window bar through the tube
157 26	1 75	Tube cooled and volume reduced On heating to near the critical point the surface now moved slowly upwards and space above became opalescent The range of temperature through which the opalescence was visible lay between 157 15 and 157 4 over the whole range of volumes investigated

In measuring temperatures by means of the thermo electric junction either of the junctions could be connected by means of a mercury switch with another junction surrounded with the vapour of bromo benzene boiling under normal pressure, the free wires being connected directly to the terminals of a

galvanometer Observations of the pressures under which the aniline in the vapour jacket surrounding the experimental tube was boiling allowing ample time for equilibrium to be established corresponding to certain readings of the barometer served to calibrate the instrument

Before filling the experimental tube mercury was introduced into it to a convenient level a bell jar was fitted round it by means of a rubber stopper and the latter was filled with a freezing mixture The capillary portion of the tube was then connected with the apparatus shown in fig 2 and the correct quantity of sulphur dioxide was introduced in the manner indicated

Third Series of Experiments with Sulphur Dioxide—In this series of experiments the same apparatus was used as in the last series but the thermo electric junction was omitted and the temperatures were determined directly from the readings of the pressures The following are the results —

T mp ratur	V l m p d by l quid in tub	M n p fl l m f b t tub	R m k
157 0	—	2 03	N p l urf m in d w ward
157 12	0 12	—	Op l b l w u f
157 3	—	—	l w p t f t b f h d b t l g l t d t uity bl
157 13	0 68	1 69	V l m d d t b l d d h t d Wh l t b lightly d ly p l t urf lm t t t y th g t mp ratur
	—	—	S rf ni h d
157 3	—	—	Opal in d d if m
157 4	—	—	l t l d
156 1	0 76	1 55	V l m d d t b l d d h t d N p l
157 07	0 79	—	
157 20	0 88	—	Op l b l q d y t g t rf
157 3	—	—	S f h d l ght d t t g w th p l y t g b t O t g pal b d ff d tl gl t t b
157 0	0 95	1 46	V l m d d t b l d d re h t d N p l
157 15	—	—	S rf ly t t p f t b m t p b t pal t

HA B AN S N P t r O d y t H M j t St M t L

(4/4)

[*From the* PROCEEDINGS OF THE ROYAL SOCIETY B VOL. 8 1906]

The Mechanism of Carbon Assimilation in Green Plants the Photolytic Decomposition of Carbon Dioxide in vitro

BY FRANCIS L. USHER AND J. H. PRIESTLEY B.Sc

[*Reprinted from the* PROCEEDINGS OF THE ROYAL SOCIETY B Vol 78]

The Mechanism of Carbon Assimilation in Green Plants the Photolytic Decomposition of Carbon Dioxide in vitro

By FRANCIS L. USHER and J H PRIESTLEY B Sc

(Communicated by Professor Morris W Travers F R S Received April 30 — Read May 10 1906)

(F om the Ch m cal d Bot n cal D p tments U ty C ll g B tol)

In a previous paper it was shown that carbon dioxide is decomposed in the green parts of plants independently of vital or enzymic activity formaldehyde and hydrogen peroxide being produced It follows from the analysis of the process of carbon assimilation there set out that this first step the photolysis of carbon dioxide should be capable of being artificially induced under laboratory conditions

It is impossible here to give even a brief account of the work of previous investigators on these lines it is sufficient to state that all experiments with chlorophyll solutions have given negative results and as regards those with other forms of chlorophyll such as dried powdered leaves or expressed juice the balance of evidence favours the view that no decomposition takes place Reference may be made to papers by Friedel† and Macchiati‡ on the positive side and by Harroy § Herzog || and quite recently Bernard ¶ who obtained only negative results Experiments with uranium compounds will be considered later

I *Experiments on the Chlorophyll Catalysis of Carbon Dioxide*

In view of the very perfect chemical and physical arrangements which assist the decomposition of carbon dioxide in the plant it is obvious that attention must be paid to these points in any experiment performed outside it It appears likely that the failure of so many attempts on the part of previous observers to carry this out has been due to a neglect of such considerations—not so much with regard to the chemical as the physical conditions The chemical conditions are those which are necessary when any other highly reversible action is being dealt with viz that one at least

R y S Pr B v l 77 p 369
† C mpt R d 1901 v l 132 p 1138
‡ B ll S B t Ital 1903
§ C mpt R d 1901 l 133 p 890
|| Z t pl y ol Chem 1902 l 35 p 4 9
¶ C mpt Re d 1905 l 140 p 509

of the products be rapidly removed from the sphere of action The physical conditions were first enunciated by Timiriazeff in the Croonian Lecture for 1903 and are as follows —(1) The optical sensitiser must be in the form of an extremely thin film and (2) the concentration of the sensitiser in this film must be so great as to ensure a large transformation of the incident solar energy within a very small space The fulfilment of both the e conditions in the case of chlorophyll in the plant is a matter of common knowledge and the experiments to be described were designed to reproduce as far as possible the essential mechanical physical and chemical arrangements which obtain in the green leaf

It should be mentioned here as the result of some observations by one of us in conjunction with Miss Irving* on the structure of the large chloroplasts of *Selaginella* and *Chlorophytum* that the chlorophyll is restricted to the exterior of the granule and that the thickness of the film is about $2\,5 \times 10^{-3}$ mm Whether this applies generally or not is of no consequence in this connection the essential point being that we have here an actual working arrangement and one which can be imitated without difficulty

The greatest possible concentration of chlorophyll is obtained when the solvent used for extracting it has been completely driven off and if material is employed which contains very little else that is soluble in the liquid in which the final solution of the chlorophyll takes place one may regard the concentration of the chlorophyll thus obtained as being approximately the same as in the plant For these experiments the material used was the leaves of grass or wheat chosen on account of their comparative freedom from fats and oils Alcohol was used for the extraction and petroleum ether for the final solution of the chlorophyll

In the first series of experiments pieces of glass plate 5×4 inches were covered with an aqueous solution of gelatine so as to form a layer 1 to 2 mm thick When set this was painted over with a solution of chlorophyll in petroleum ether or benzene In this way a fairly uniform film of chlorophyll is obtained and if when the plate is placed in carbon dioxide light is allowed to strike it in the direction → carbon dioxide → chlorophyll → gelatine we have a reproduction of the essential features of the arrangement in the living cell Measurements of the thickness of the chlorophyll film gave an average value of about 6×10^{-3} mm

On placing plates prepared in this manner in a bell jar containing moist carbon dioxide and exposing to light the chlorophyll in the course of a few hours became completely bleached and the gelatine developed a red

* At present unpublished

colour when immersed in a solution of rosaniline decolourised with sulphurous acid. The experiment was repeated several times with the same result and when performed on a larger scale the distillate from an aqueous solution of the gelatine was found to contain formaldehyde the substance being identified by the characteristic methyleneaniline and tetrabromo hexamethylenetetramine reactions The melting point of the methylene aniline was within 2 of that of the pure substance It will be seen that the action which takes place under these conditions is the same as that which occurs in a green plant when the protoplasm has been killed and the enzymes destroyed the accumulation of formaldehyde is possible so long as any chlorophyll remains to remove the hydrogen peroxide The use of gelatine may be avoided by a modification of the arrangement just described A layer of water in a shallow porcelain dish replaces the gelatine and the chlorophyll film is obtained by dropping the petroleum ether solution over the surface from a pipette at the same time directing a current of air against it so as to evaporate all the solvent before the chlorophyll can collect in patches Experiments performed in this manner gave the same results as those with the gelatine films The latter are more convenient to manipulate but it is preferable to dispense with the gelatine if the object is to collect as much formaldehyde as possible since this substance has a larger concentration in the residue than in the distillate

A second series of experiments was undertaken with the object of ascertaining whether the process could be carried as far as the evolution of gaseous oxygen It has already been pointed out in a previous paper that the decomposition of the hydrogen peroxide in the plant is brought about by an enzyme probably a catalase and it was also shown that a certain amount of oxygen can be evolved from plants which have been killed provided that the enzymes are not destroyed

The catalase employed was obtained from sheep s liver by extracting the dried and powdered material with water containing a little thymol the enzyme being precipitated by excess of absolute alcohol The arrangement of the experiments was the same as in the first series but the gelatine was made up with an aqueous solution of the catalase instead of with pure water and the solution thus prepared was spread upon a strip of tinned iron 60 cm long and 3 cm wide After painting it over with chlorophyll solution the strip was placed inside a glass tube sealed at one end just large enough to contain it and which was afterwards drawn out at the open end to a capillary and sealed to a T piece connecting it through two stop cocks with a supply of carbon dioxide and a pump The carbon dioxide used was passed over red hot copper in order to remove traces of oxygen and the tube was

exhausted and refilled six times A similar tube without any catalase was treated in the same way When the tubes had been filled with oxygen free carbon dioxide for the sixth time they were sealed off at the capillary portion and exposed to sunlight In the course of an hour the gelatine in the tube containing the enzyme was swollen with bubbles of gas and the chlorophyll film became distorted and broken up The only visible change in the other tube was the bleaching of the chlorophyll When the tubes had been exposed to light for two days they were attached to a Topler pump by a short piece of rubber pressure tubing After completely exhausting the system on the pump side of the capillary the latter was broken off inside the pressure tubing and the gas pumped out through a tube packed tightly with soda lime which absorbed all but a trace of the carbon dioxide The tube containing the catalase yielded 0 6 c c of oxygen with a trace of nitrogen while the other gave a minute bubble of nitrogen only the latter being derived in each case from the air present in the carbon dioxide before its passage over the red hot copper Two more similar experiments gave 2 c c and 1 2 c c of oxygen respectively

It was found that if the exposure to light was continued until the chlorophyll was bleached the enzyme was poisoned by the accumulating formaldehyde This is precisely what occurs in the plant under similar conditions that is when the protoplasm only has been killed

According to the analysis of the photosynthetic process given in the paper already referred to where it was shown that the condensation of formaldehyde to carbohydrates is dependent upon the healthy condition of the protoplasm one would expect non chlorophyllous living cells to be able to bring about this change It appears from the feeding experiments of Bokorny Bouilhac and Tréboux that light is necessary in the case of green plants and we have found that this is also the case with the white petals of *Saxifraga Wallacei* which are capable of forming starch in the light from a 0 001 per cent solution of formaldehyde though no condensation takes place in the dark In a further series of experiments these petals when quite free from starch were painted with chlorophyll solution and floated on water charged with carbon dioxide in a bottle placed in the light In the course of a day they were found to contain starch In this case we have what is essentially a green leaf arranged in a different way though it is of course a very inefficient substitute for the natural organ

As it was of interest to ascertain whether formic acid is actually produced as an intermediate product in the photolytic reduction of carbonic acid to formaldehyde an experiment similar to those described in Series I above was performed the gelatine being dissolved in a solution of sodium bicar

bonate In this case the whole of the bicarbonate was converted into formate When neutral or slightly acid gelatine was used no formic acid could be detected With very large concentrations of carbon dioxide formic acid appears to be the sole product since when sealed tubes containing chlorophyll water and liquid carbon dioxide were exposed to light no formaldehyde was found though a considerable quantity of formic acid was produced

If however formic acid is an intermediate product in the photolysis of carbon dioxide in the plant the latter should be able to build up carbohydrates from this substance. This was found to be the case with *Elodea* which when exposed to light in a 0 02 per-cent. solution of formic acid gave off oxygen and formed starch no starch was formed or oxygen evolved from *Elodea* kept in the dark carbon dioxide being carefully excluded in each case When the plant was previously killed the same changes took place as when carbon dioxide was used that is to say the chlorophyll became bleached and the plant was subsequently found to contain formaldehyde.

II *The Photolytic Decomposition of Carbon Dioxide in the Presence of Uranium Compounds*

In a previous paper to which reference has been made above it was stated that Bach s observations had been repeated and confirmed in the case of uranium acetate minute quantities of formaldehyde being found in the distillate. Since then our attention has been called to a recent paper by Euler * who was unable to confirm Bach s observations A more detailed investigation has therefore been made and since it cannot be proved that any particular organic substance which may be produced is formed from the carbon dioxide and not from the electro negative portion of the organic salt when the latter is employed a purely inorganic sensitiser has been used in the present series of experiments.

In the first of these which was a repetition on a larger scale of one which has already been described a large Pettenkofer tube was filled with a litre of 2 per cent. uranium sulphate solution and a slow current of carbon dioxide was passed through it the whole apparatus being placed on the roof in order to utilise all the available sunlight Within an hour of passing the carbon dioxide the contents of the tube were considerably turbid and at the end of the exposure which lasted from January 27 till February 9 the precipitate amounted to several grammes and was of a pale violet colour The greater part was soluble in acetic acid and was found to be a mixture of uranous

* B r d t. h m G s 1904 ol 3 p 3415

and ordinary uranic hydroxides The insoluble residue* was a hydrate of uranium peroxide being characterised by its insolubility in acetic acid and also by the fact that it imparted a brownish red colour to a solution of titanium oxide in sulphuric acid The filtrate from the mixed hydroxides was distilled and the distillate was examined for formaldehyde None however was found though the liquid energetically reduced Fehling s solution and silver nitrate It was subsequently found to contain formic acid the lead salt of which was prepared and identified The undistilled residue was then evaporated down at 100° and when nearly solid was repeatedly extracted with dry ether in order to remove any formic acid which had not evaporated The residual solid was extracted with absolute alcohol and the solution on evaporation left a small quantity of a brown syrup bitter to the taste which reduced Fehling s solution When treated with phenylhydrazine acetate no crystalline derivative could be separated nor could the syrup itself be induced to crystallise On account of its appearance taste and reducing action it presents a striking resemblance to the substance obtained by Butlerow† from formaldehyde and milk of lime and called by him methylenitan It has been shown that formaldehyde when allowed to stand for some time in presence of uranic hydroxide gives rise to a substance with similar properties It does not appear possible to make any more explicit statement with regard to the identity of the substance produced from carbon dioxide in the manner described with methylenitan since it is produced only in minute quantities and does not admit of purification or of the preparation of a derivative which can be purified it is however worth while to notice that as regards the two substances produced by the action of light on carbon dioxide in the presence of uranium sulphate on the one hand and by the condensation of formaldehyde by uranic oxide on the other

(1) They are both organic substances which char on heating
(2) Both are insoluble in dry ether and soluble in water and alcohol
(3) Both have a bitter taste and reduce Fehling s solution
(4) Neither reacts with phenylhydrazine

Since it was conclusively proved by this experiment and those which preceded it that formic acid is one of the products of the action of sunlight on carbon dioxide and in view of the fact that the quantity of any product formed is materially influenced by the concentration of the substance giving rise to it—which is necessarily small when that substance is carbon dioxide—it was thought that some light would be thrown on the reaction if one started with

* UO_4 dissolves slowly in acetic acid if uranous compounds are present
† 'Comptes Rendus, vol 53 p 145 Liebig's Annalen vol 120 p 296.

formic acid instead of with carbon dioxide For this purpose a solution of uranyl formate was employed and the method has the advantage that any removal of formic acid from the system is indicated by a corresponding precipitation of uranic hydroxide The uranyl formate for these experiments was prepared by heating uranyl nitrate (obtained from Kahlbaum) until oxides of nitrogen were no longer evolved and dissolving the residual uranic oxide in the least possible quantity of 5 per cent formic acid Preliminary experiments were carried out in order to ascertain whether any visible change takes place when the solution is exposed to sunlight It was found that on placin a flask containing it in the light the liquid became turbid after about 10 minutes' exposure and in half an hour a considerable precipitate had accumulated The precipitate at first produced is of a pure yellow colour and consists of ordinary uranic hydroxide After a short time it becomes violet coloured and when a considerable quantity has collected consists of a mixture of uranic and uranous hydroxides together with small quantities of uranium peroxide As in a large number of experiments no formaldehyde could be detected several experiments were performed with a view to ascertain whether any gaseous products were formed In one of these a glass tube about 30 cm long and 2 cm bore was half filled with a solution of uranyl formate drawn out to a capillary exhausted and sealed After four days exposure to sunlight the tube was connected with a Topler pump and about 50 c c of gas were collected which on analysis was found to consist of approximately equal volumes of carbon dioxide and hydrogen This experiment was repeated several times with the same result though the carbon dioxide and hydrogen were not always produced in the same proportions It should be stated that any uranium salt which remained in solution was invariably reduced to a green uranous compound and this no doubt accounts for the variations observed in the relative volumes of the two gases

The foregoing experiments show that carbon dioxide in the presence of uranium compounds gives rise under the influence of light to formic acid and that formic acid under the same conditions gives rise to carbon dioxide and hydrogen It is probable for reasons which will appear later that we are dealing with several consecutive reactions which under the conditions of the experiments have widely different velocities and which are not strictly reversible If this be so it follows that it will be very difficult if not impossible to isolate certain intermediate products For example in the case of the first series of experiments with uranium sulphate it may be questioned whether the formic acid found really represents the first stage in the photolytic decomposition of carbon dioxide it may quite possibly be the final product of a reaction between formaldehyde and one of the hydroxides

present following on the primary reaction which gave rise to the formaldehyde and having a much higher velocity In such a case one could not expect to find formaldehyde in the final mixture As the question at issue is whether or not formaldehyde is produced at any stage in the series of reactions which take place when sunlight acts on carbon dioxide under the conditions described and as it was found that formaldehyde could not in any way be isolated from the mixture it appeared that a careful study of the reactions of formic acid and aldehyde with such substances as were formed under the conditions of the experiments was the method most likely to settle the question It may be worth while to point out here that a careful distinction must be maintained between those reactions which are endothermic and derive the necessary energy from the sunlight and those in which the action of light is purely catalytic

Solutions of uranium salts—especially those like the formate—have always an acid reaction and are probably hydrolysed to a considerable extent so that any hydrogen peroxide that is formed is not completely removed from the system but remains in equilibrium with the difficultly soluble uranium peroxide We have therefore to consider reactions which may occur between

(i)	Formic aldehyde	*and*	uranium peroxide
(ii)	acid		
(iii)			hydrogen
(iv)	aldehyde		
(v)			uranic oxide

It has been shown by Geisow* that when hydrogen peroxide reacts with solutions of formaldehyde in neutral or acid solution hydrogen and carbon dioxide are the sole products no formic acid being produced On the other hand the peroxides of lead and manganese give hydrogen and a metallic formate It has been found that uranium peroxide reacts in the dark with formaldehyde and that hydrogen and uranium formate are produced but no carbon dioxide Hence in such a system as the one under consideration where there is a constant but very small concentration of hydrogen peroxide there is the possibility of explaining the production of both hydrogen and carbon dioxide the reaction taking place between the formaldehyde and hydrogen peroxide though of course at the expense of the uranium peroxide and this appears to be the probable explanation when we consider that the velocity of reaction in the case of hydrogen peroxide must be very much greater than in the case of uranium peroxide The fact that hydrogen and

* Ber deut chem Ges 1904 vol 37 p 515

carbon dioxide are formed as the result of the interaction of hydrogen peroxide and formaldehyde is a piece of evidence which strongly supports the view that the latter substance is formed in the experiments we are considering provided that formic acid does not give rise to these gases under similar conditions As no record of experiments on these lines could be found the point was investigated The mixture of formic acid and hydrogen or uranium peroxide was placed in a Zeisel flask with a condenser attached This was first connected with some bulbs containing lime water and a current of CO_2 free air was passed through the apparatus while the mixture was heated on a water bath Considerable quantities of carbon dioxide were evolved as shown by the precipitation of calcium carbonate A fresh quantity of the reaction mixture was then taken and the apparatus connected with a Schiff s nitrometer while a current of carbon dioxide was passed Not a trace of hydrogen was evolved although the mixture was boiled for three hours There is apparently no difference between the reactions in the case of hydrogen peroxide and uranium peroxide except that the latter proceeds more slowly These experiments were carried out in the dark

Experiments with ordinary uranic oxide showed that formaldehyde reduced it both in the dark and in the light uranous oxide and a formate being produced but only in the light was the violet colour observed It appears that this coloration is merely a surface effect since the precipitate when dissolved in acid and reprecipitated has the ordinary black colour of uranous oxide

The following experiments bring out rather more clearly the distinction between formic acid and aldehyde mentioned above —

To one of two tubes containing pure uranium peroxide a dilute solution of formaldehyde was added to the other some dilute formic acid After exposure to light from February 16 to February 19 no effect was visible in the tube which contained formic acid whereas the other contained uranous formate and a violet coloured precipitate In order to examine the gases produced in the two cases two more tubes were prepared one of which (*a*) contained uranium peroxide formic acid and formaldehyde while the other (*b*) contained uranium peroxide and formic acid only Both were drawn out to a capillary exhausted and sealed They were exposed to light from February 27 till March 6 when the gases were pumped out and examined (*a*) contained 4 8 c c of carbon dioxide and 4 8 c c of hydrogen while (*b*) contained 9 8 c c of carbon dioxide and no hydrogen

There is thus no direct experimental evidence that formaldehyde is produced under these conditions, that is to say it has not been isolated and

identified but there is indirect evidence of its formation at some stage Whilst hydrogen is always found among the products of the action of light on carbon dioxide in the presence of uranium compounds under no conditions in any way approaching those of the experiments in question has hydrogen been obtained from formic acid The reduction of uranic oxide or of uranium peroxide to a violet coloured lower oxide which was always observed in the experiments with carbon dioxide can again only be brought about by formaldehyde whilst the formation of a substance with the properties of methylenitan which has only been prepared from formaldehyde furnishes additional support to this view

Summary

I —(1) Photolytic decomposition of aqueous carbon dioxide can take place in the presence of chlorophyll independently of vital or enzymic activity provided that the necessary physical and chemical conditions are strictly adhered to

(2) The products of the decomposition are formaldehyde and hydrogen peroxide formic acid being an intermediate product

(3) It is possible to reconstruct the process of photosynthesis outside the green plant (*a*) as far as the production of formaldehyde and oxygen by introducing a suitable catalysing enzyme into the system and (*b*) as far as the production of oxygen and starch by introducing in addition to the enzyme certain kinds of non chlorophyllous living protoplasm

II —(1) There is direct experimental proof that formic acid is a product of the photolytic decomposition of carbon dioxide in the presence of an inorganic uranium salt

(2) Formaldehyde has not been isolated and identified in the case of an inorganic uranium salt but a study of the reactions involved favours the view that it is formed as a transitory intermediate product

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17 (4/5)

Über die Löslichkeit von NO in wasserigen Losungen von $FeSO_4$ $NiSO_4$ $CoSO_4$ und $MnCl_2$

V

Francis L. Usher

Die Absorption von NO durch Ferro ulfatlosungen ist kurzlich von Manchot und Zechentmayer[1]) quantitativ verfolgt worden ebenso von Hufner[2]) der seine Untersuchungen auch auf $NiSO_4$ $CoSO_4$ und $MnCl_2$ Losungen erstreckt hat Diese Untersuchungen ergaben ziemlich weitgehende Aufschlusse uber die Abhangigkeit der absorbierten Menge Stickoxyd von dem Drucke des Gases unter verschiedenen Bedingungen sie haben aber nicht die Natur und die Konstitution der Stickoxyd Eisenverbindung sicher gestellt sondern nur die Tatsache dass die Grenze der Absorption erreicht ist wenn das Eisen und das Stickoxyd in molekularem Verhaltnis verbunden sind Es schien moglich und wahrscheinlich die Natur dieser Verbindung durch Beobachtung der Gefrierpunktserniedrigung von $FeSO_4$ Losungen verschiedener Konzentration die mit NO unter verschiedenem Druck gesattigt sind sicher zu stellen Besonders ergibt sich die interessante Frage ob eine Verbindung mit dem undissociierten Salzmolekul oder ein Eisen enthaltendes komplexes Kation oder vielleicht auch Anion entsteht

Nach vielen Versuchen ergab sich die Unmoglichkeit uberein stimmende Resultate nach dieser Methode zu erhalten weil weder der Druck des NO noch der Gefrierpunkt der Losung konstant war obwohl das Volumen der Losung und des ganzen Apparates konstant blieb und fur ausreichende bestandige und wirksame Ruhrung der Losung gesorgt war Ein solches Resultat bedeutet offenbar das zwischen den beteiligten Stoffen chemische Einwirkung stattfindet. In der Tat ergab sich nach vollstandiger Entfernung des NO aus der Losung dass diese eine zwar kleine aber doch nachweisbare Menge Eisenhydroxyd enthielt. Weder Manchot und Zechentmayer noch Hufner machen

[1]) Leb A n 350 368 (1906)
[2]) Z ts hr f phys k Ch m e 59 416 (1907)

daruber eine Bemerkung, erst spater fand ich in einer Arbeit von J W Gray[1]) („Uber das Atomgewicht des Stickstoffs") die Bemerkun dass NO durch $FeSO_4$ Losungen teilweise zu Stickoxydul und Stick stoff reduziert wird

Da es mir so unmoglich war mit $FeSO_4$ Losungen genaue Resul tate zu erhalten, wollte ich die Beobachtungen Hufners verwenden, dass das NO eine ahnliche, jedoch farblose Verbindung mit $NiSO_4$ bildet In diesem Falle brauchte ich nicht zu furchten, dass in dei Losung eine Oxydation stattfinden konnte

Ein vorlaufiges Experiment mit einer ziemlich konzentrierten $NiSO_4$ Losung ergab eine ausnehmend kleine Absorption von NO, und nach mehrern sorgfaltigen Experimenten zeigte sich das Resultat, dass $NiSO_4$ und ebenso auch $CoSO_4$ und $MnCl_2$ sich wie vollstandig indifferente Salze verhalten und im Gegensatze zu den Beobachtungen Hufners die Loslichkeit von NO in Wasser veimindern, also einfach wie andeie Salze aussalzend wirken

Experimentelles

Die Absoiptionskoeffizienten wurden mittels des gewohnlichen Appa rates nach Ostwald bestimmt Die ersten Experimente wurden mit einem kleinen Absorptionsgefass von 47 25 ccm Inhalt gemacht, bei welchem der maximale Fehler in den Beobachtungen etwa 3% be trug Die spatern Versuche wurden mit einem grossern Gefass von 246 31 ccm ausgefuhrt, und der maximale Fehler in den Beobachtungen war hier nur 0 5% Fin Thermostat wurde nicht angewendet, weil die Zimmertemperatur sich wahrend des Experimentes niemals mehr als 0 2° uber oder unter 20° anderte Es ist zu bemerken, dass die ge zogenen Folgerungen nur auf dem Vergleich von unter ahnlichen Be dingungen angestellten Experimenten und auf Unterschieden, die den grosstmoglichen Beobachtungsfehler uberschreiten, basieren

Zur Darstellung des Stickoxyds wurden einige Methoden versucht und zum Schluss die Winklersche Methode[2]) benutzt, welche aus Jod wasserstoff und salpetriger Saure das reinste Gas liefert Das nach der Emiehschen Methode[3]) aus Quecksilber und mit Kaliumnitrit gesattigter Schwefelsaure dargestellte Stickoxyd war manchmal reiner als das nach der Winklerschen Methode, doch veranderte sich seine Qualitat von Zeit zu Zeit

[1]) Inaugural Dissertation Bonn 1907 gedruckt bei Emil Eisele
[2]) Ber d d chem Ges **34**, 1408 (1901)
[3]) Monatshefte f Chemie **13**, 73 (1892)

Die folgenden Zahlen geben das Volumen Stickoxyd (reduziert auf 0° und 760 mm *Hg*) in ccm an das von den betreffenden Flussigkeiten bei 20° absorbiert wird

	Lösu g	Abso p t n k ff	B m k ngen
Kl e Gefass	Was	0 049	
	N SO (*H fners* K trat n)	0 018	D rst ll g nach *W kler* *NO* m t h lil ge ge wasch n
	FeSO (on *Hüfners* Kon tration)	0 180	
→)	Was	0 074	
	N SO (g sättigt b i 20)	0 0245	
	CoSO (	0 0 88	
	MnCl ( )	0 0082	
→	Was	0 07o3	
G ss s Gefäss	Was e	0 04 1	D rst ll g n h *W nkler* *NO* m t k t t S hw f l ä e gewaschen
→		0 0449	
→		0 0448	
→		0 0468	D t llu g n h *W kler* *NO* m t h l l ge g was h
→		0 0471	
→		0 0473	
→		0 0487	

Die Tabelle zeigt d iss sich der Absorptionskoeffizient des Stick yds von Experiment zu Experiment andert, obwohl das Gas bei allen i der gleichen Weise dargestellt wurde und dass vergleichbare Resul te nur dann erhalten werden konnen wenn man bei jeder Experi mentenserie fur welche ein gewisses Gasquantum erzeugt worden war die Loslichkeit in Wasser zum Vergleich immer wieder von neuem be stimmt. Dies berucksichtigend kommt man zu dem Resultate dass von den vier von Hufner studierten Salzen nur das Ferrosulfat eine ausnahmsweise Wirkung hervorbringt die ubrigen drei nicht Hufner aber grundet seine Folgerungen auf die Annahme dass der Absorptions koeffizient seines Stickoxyds immer denselben Wert behielt namlich wie von Winkler angegeben 0 04706 Nun gibt Gray an was schon Gay Lussac beobachtete und Emich) bestatigte dass Stickoxyd sehr leicht durch Kalilauge teilweise unter Bildung von Stickoxydul und Stickstoff zersetzt wird auch wenn es nur ein einziges Mal durch

) D Pfeil bede t t d f d f lg de E p m t e f sche Me ge *NO* e e gt w d

) M tshefte f Ch m e **13**, 90 (1892)

geleitet wird Ich vermute dass die Resultate Hufners dadurch wert los werden Jedenfalls ist es merkwurdig, dass das mit konzentrierter Schwefelsaure gewaschene Stickoxyd einen kleinern Absorptionskoeffi zienten hat als das mit Kalilauge gewaschene

Dass Stickoxyd durch Ferrosulfatlosungen wirklich reduziert und dadurch sein Volumen vermindert wird, ergibt sich klar aus folgenden Zahlen, die das mit der Zeit veranderliche von einer etwa $^1/_{10}$ normalen Ferrosulfatlosung aufgenommene Volumen Stickoxyd angeben

Sonnabend	10 15 vorm	36 2 ccm
	11 45	36 5
	12 15 nachm	36 7
	12 35	36 9
	4 05	37 3
Montag	12 45	38 8
Dienstag	12 05	39 6

Die erste Zahl, 36 2 ccm kann als die eigentliche einfache NO Absorption genommen werden, die weitern kleinen Zunahmen in der Absorption haben dann ihren Grund in der Reduktion zu N_2O und N, und zwar belauft sich die weitere Absorption bis auf 9 % der absor bierten Menge

Schliesslich kann die von Hufner angegebene Gleichung

$$v = a + bp$$

die Beziehung zwischen der absorbierten Menge Stickoxyd und seinem Druck nicht exakt darstellen, wenn die Stickoxyd Ferroverbindung in der Losung teilweise dissociiert ist Sie muss vielmehr parabolisch sein, und zwar von der Form

$$v = \frac{ap(K + A) + a^2p^2}{K + ap},$$

wobei a den Absorptionskoeffizienten von Stickoxyd in Wasser, p den Partialdruck des reinen Stickoxyds im dargestellten Gas, A die Gesamt konzentration des Eisens in der Losung und K die Dissociationskon stante der Verbindung des Eisensalzes mit dem Stickoxyd bedeutet, unter der Voraussetzung, dass diese Verbindung aus je einer Molekel ihrer Bestandteile besteht, und die aussalzende Wirkung des Eisensalzes vernachlassigt wird

Prag K K deutsche Universität Phys chem Institut (Prof Dr Rothmund)

18 (4/6)

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431 Sir William Ramsay und Francis L Usher
Über die Einwirkung der Radium Emanation auf die Elemente der Kohlenstoffgruppe

BERLIN 1909

431 S r William Ramsay und Francis L Usher
ber die Ehnwirkung der Radium Emanation auf die Elemente der *Kohlenstoffgruppe*

(E g g m 23 J h 1909)

Schon Ende M r hat der e e vo uns e n ge Res ltate ber ben Gegenstand de Che n cal Soc ety m tget lt (Tra s 95 694) wir die Unters chu g fo tg f h t habe l alte w es f or teilhaft, die Lrgebni se se e Ve che h e sam e stellen

Die Art u d We se de Ve s hsa sf hr ng war fol e de D e Emanation w rde aus e er 0 2111 g metall ches Rad um e thaltende Losung von Rad un brom d san t lem begle te le K llgas a ge pumpt die wahrend e e Woche er e gte M ge von Gas bet g fast genau 25 ccn und e th elt 0 0912 cm Eman t o N cl de Explosion bl eb etwa e n halbes K b k e ta eter ab g dieses w d an einem kleinen mit geschmol e em u d t Wasser befe cl tete Kali überzogenen Glasrohrche gesammelt N ch e er St de w de das von Kohlensa re bef e te Gas n e lee gep mptes Glask lbcl e eingeführt welches d ejen ge L s ng e th elt de e Bee fl ss g durch die Ema t on gep ft we de sollte D d e Halblebe sper od der Emanat on 3 86 Tage bet gt w de ler I l alt d s K lbche s sich selbst wahrend vier Wochen ube lassen l d eser Ze t a t d e Energ e de Ema at on fast erschopft D e Gase wurde al d a ab gepumpt u d a alys ert

Folge de Tabelle g bt d e Res ltate der Ve suche

L g	V l d Em t mm	N m	O m	CO m	CO	K ll g e m	H m
H S F q	0 0724	—	—	0 063	—	9 1	1 03
T (SO) q	0 0912	0 210	—	0 0 4	0 096	—	0 69
Z (NO) q)	0 069	0 76?	—	0 116	0 008	—	—
)	0 0865	0 456	—	0 124	0 00?	—	—
Th (NO) q)	0 1120	3 686	—	0 5 1	—	—	—
))	0 0765	0 639	—	0 124	—	—	—
Pb (ClO) q	0 0649	—	9 6 5	0 007	0 006	2 031	—

Diese Res ltate s d u te so angeor l et d ß d e Menge Kol l stoff welche von e em K b km ll n eter Ln a at n he r h t t b ll Asch gegeben w d

) D e N trat h b st t St ko yd g l f t w l h s ach Z t unbestimmt n M g S t ff d h Q l lb b b tw d h m die A aly fuh t

?) D M g d Em t t h e h h h h h h g h t t

Losung von	H_2SiF_6	$Ti(SO_4)_2$	$Zr(NO_3)_4$		$Th(NO_3)_4$		$Pb(ClO_3)$
			I	II	I	II	
Kohlenstoff	0 518	0 982	1 071	0 873	2 93	0 968	0 102 mg.

Es sei hier bemerkt daß salpetersaures Quecksilberoxydul keine Spur von Kohlensaure oder Kohlenoxyd geliefert hat

Aus den obigen Ziffern ist ersichtlich daß die Elemente der Kohlenstoffreihe ohne Ausnahme Kohlenstoffverbindungen unter der Einwirkung der Emanation liefern die erzeugten Mengen sind jedoch nicht alle gleich Es ist nicht unwahrscheinlich daß die jenigen Elemente welche ein hohes Atomgewicht besitzen im allge meinen leichter spaltbar sind als diejenigen mit niedrigerem Atom gewicht doch laßt sich vermuten daß Blei besonders stabil ist und wenig Tendenz besitzt sich in Kohlenstoff zu verwandeln

Ahnliche Versuche mit Verbindungen anderer Elemente sind im Gang

London University College, 21 Juli 1909

III.—*The Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water.*

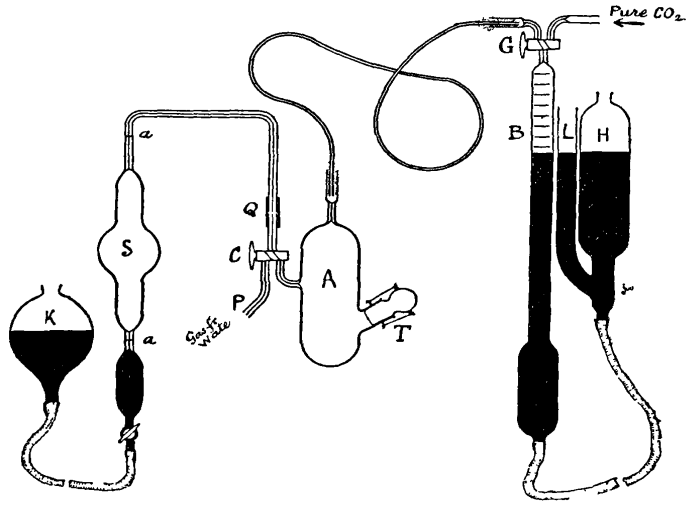
By Francis Lawry Usher.

The object of the investigation to be des r bed in this paper was to place upon record a larger numbe of accu ate measurements of the solubility of a gas in solutions of non el t olytes than has hitherto been available. Although the e is a considerable mass of experimental data relat ng to the solubility of gases in salt solutions, the non-electrolytes examined have been confined to some sugars, chloral hydrate, carbam de, and a few sl ghtly d sociated organic acids (Roth, *Ze t ch plys k l Cl em* 1897, **24**, 114; Braun, *b d* 1900, **33**, 721; Knopp, *b d* 1904, **48**, 97; Christoff, *bid* 1905, **53**, 321; Hufner, *ib d* 1906, **57**, 611; Steiner, *Wied Annal n* 1894, **52**, 275). The experiments re o ded here were all carr ed out at 20°, and ex ept in the case of suc o e at only one concentration, n mely, s mi no mal. The gas used was carbon dioxide, hosen because its ompa at ely la ge absorption-coeffi ient permitted g eater a uracy in the deter minations, whilst at the same t me its light de ti n from Henry's law is not sufficient to pr clude its use as an ind ffe ent. The substances studied were sucrose, dext ose, mann t l, gly ine, pyro gallol, quinol, catechol, resorcinol, carbamide, th o arbamide, urethane, acetamide, antipyrine, acetic acid, and *n*-propyl al ohol.

Experim ntal.

Except in the case of the two liqu d substances examined, namely acetic acid and *n*-propyl al ohol, the s lut ns were of exactly semi normal strength, and were prepa ed in the absorption vessel itself. The apparatus was designed with this end in v ew, and a desc ption of it will now be given. The a bon dioxide was prepared in an ordinary Kipp's apparatus f om ma ble whi h had been boiled for some time in distilled water in o der to remo e adhering and occluded air, and conc nt ated hydrochloric a id. The gas was found to contain less than 0·03 per cent. of foreign gas. The outlet tube from the K pp s apparatus was connected through a tap with a large U-tube filled with marble chips, which served to prevent any acid spray from be ng carried o e with the carbon dioxide. The gas was next led through a wash-bottle containing concentrated sulphuric acid, and finally through a phosphoric oxide tube. Whe ever practicable, connex ons between glass port ons of the apparatus were made by sealing the glass together w th a

mouth blowpipe in fact the number of taps and rubber connexions was kept as small as possible and the latter when it was necessary to use them consisted of short pieces of pressure tubing of small bore inside of which the glass ends were brought together The tap of the Kipp s apparatus was left permanently open so that the internal gas pressure was always in excess of the atmospheric and no air could leak into the apparatus The measuring burette (*B*) was of 100 c c capacity Of this 50 c c were contained in the narrow upper part which was graduated in tenths of a c c and was calibrated by weighing out mercury whilst the



remaining 50 c c were contained in a bulb blown below this graduated portion The burette was connected by rubber tubing with a mercury reservoir *H* carrying a levelling tube *L* of the same diameter as the graduated part of the burette and was provided at the top with a three way tap *G* by means of which it could be connected either with the carbon dioxide supply or with the absorption vessel The absorption vessel *A* was of about 200 c c capacity and was provided near the bottom with a tubulure *T* about 14 mm wide carrying two small glass hooks and which could be closed by a ground glass stopper carrying a second pair

or hooks by means of which it could be held firmly in po it o i with two elastic bands The solid substance was introduced through this tubulure On the opposite side and nearer the top was a short capillary tube car ying a three-way t p C so arranged that either the abs pt on vessel could be c nnected with a vessel S delivering a known volume of gas f ee water or the latter could be conne ted independently of the absorption vessel with the store of gas free water employed

A flexible copper cap llary 2 metres long and of 1 5 mm bore was us d to onne t the absorption vessel w th the burette and was cemented into the glass tubing with marine glue the junctions being sub equ ntly en losed in plaster-of Paris blocks to prevent them from becom ng l ose when the absorption vessel was shaken A thermostat was mployed for all the expe iments which were carried out at 20 $\pm$0 02 When the room temperature rose above 20 a cool ng co l w s ntroduced into the thermostat The method of carrying out a determination is as follows

In the fi t pla e a semi no mal solution of the substance to be examined was pr pared and its specific gravity at 20 was deter mined and fr m this was calculated the weight of substan e wh ch would give a sem normal solution when diss lved in 117 c c of water this be ng the am unt of water used in eve y case The exact quantity of the substan e was then we ghed into the dried abso pt on vessel thr ugh the tubulu e after wh ch the stopper was inserted and fasten d in pos tion The absorption vessel was now connected through the three-way t p with a Topl r pump and completely exhausted After los ng the tap it was fill d with pure d y arbon dioxide by alternately filling the burette from the supply and allowing the g s in the burette to pass into the absorpti n ve sel by suitably turn ng the three way tap G The abso ption vessel was now placed in the thermostat and left there until the tempe atu e of the contained gas was constant at 20 and it was arrang d that when it was full of gas at 20 under the atmospheric p essure the le el of the mer ury should be near the top of the bu ette The burette r ading was then observed and the room temper ti re and ba omet c height noted Pure gas-fre water had now to be int oduced Ordinary di tilled water was used and was p e ously boiled out in a vacuum in a round bottomed flask provided with a rubber st pper carrying two glass tubes one short the other passing to the bottom of the flask As soon as all air had been completely remo ed the flask was closed cooled to a little below 20 and the longer tube was then connected with the branch P of the three way tap C and so with the vessel S which was filled with mercury and of which the volume between

two marks on the capillary stem at a and a' was accurately known this was 117 0 c c at 20° By suitable manipulation all air was removed from the capillary tubing and the tap C was now turned and the vessel S filled with gas free water to the lower mark a' C was next turned in the other direction and by raising the reservoir K and lowering the reservoir H the exact quantity of water contained between a and a' was driven into the absorption vessel C was now closed and the absorption vessel disconnected at P and Q and placed in the thermostat It was then shaken vigorously until all the solid was dissolved and the resulting solution saturated with carbon dioxide at 20° under the atmospheric pressure When the burette reading was constant the barometer height and room temperature were again noted and the determination was now finished Care was taken that no gas or liquid passed back from the absorption vessel to the burette consequently the gas in the burette was always dry whilst that in the absorption vessel was only dry at the commencement of the experiment For the purposes of calculation the volume and hence the densities of the solid substances had to be known The values of some of these were taken from papers by Schrodter (*Ber* 1879 **12** 1611 1880 **13** 1070) and some were redetermined

The absorption coefficients for the liquids acetic acid and n-propyl alcohol were determined by Ostwald s method in an absorption vessel containing 246 3 c c Since the volume of gas absorbed in the case of these liquids was much greater than the capacity of the burette the latter had to be refilled several times Although the error of reading was repeated as often as the burette was filled the volume of gas dealt with was proportionately larger and the probable error in the final result therefore remained the same as for the other solutions for which a single filling of the burette sufficed

Two determinations were carried out with every solution examined and four in the case of water The maximum difference between the results of two such experiments was 1 in 250 whilst most agreed to within 1 or 2 in 1000

Calculation of Results

The absorption coefficients (α) given represent the volume of carbon dioxide reduced to 0° and 760 mm which is dissolved by 1 c c of liquid at 20° when the partial pressure of the carbon dioxide is 760 mm

(1) Calculation of absorption coefficient for solutions of solids

Let x = volume of absorption vessel up to beginning of copper capillary

Let y = volume from beginning of c ppe capillary to m rk 0 on burette

b_1 and b_2 = initial and final burette read ng

A = v lume of solution

a = volume of solid subst nce

P = barometric height cor ected to 0

p = vapour pressure of sol tion at 20

t = room temperature

The corrected initial volume of gas in the apparatus will be

$$\frac{P}{760}\left\{(x-a)\ \frac{273}{293} + (b_1+y)\ \frac{273}{273+t}\right\}$$

and the orre ted final volume w ll be

$$\left\{\frac{P-p}{760}(x-A)\ \frac{273}{293} + \frac{P}{760}(b_2+y)\ \frac{273}{273+t}\right\}$$

hence the volume dissolv d by A c c of the solution

$$= \frac{P}{760}\ \frac{273}{273+t}(b_1-b_2) + \frac{273}{293}\left\{\frac{P}{760}(x-a) - \frac{P-p}{760}(x-A)\right\} \text{c c}$$

and

$$a = \frac{\frac{P}{P-p}\ \frac{273}{273+t}(b_1-b_2) + \frac{273}{293}\left\{\frac{P}{P-p}(x-a) - (x-A)\right\}}{A}$$

If the room tempe ature i itself 20 the express on s mplifies to

$$a = \frac{\frac{273}{293}\left\{\frac{P}{P-p}(x-a+b_1-b_2) - (x-A)\right\}}{A}$$

(i) When wate is u ed instead of a s lution of a sol d if W is the volume of water taken

$$a = \frac{\frac{P}{P-p}\left\{\frac{273}{273+t}(b_1-b_2) + \frac{273}{93}x\right\} - \frac{273}{293}(x-W)}{W}$$

or

$$= \frac{\frac{273}{293}\left\{\frac{P}{P-p}(b_1-b\ +x) - (x-W)\right\}}{W}$$

if the room tempe ature i 20

(iii) In th cas of the solutions of liquids examined the absorption coefficient me u ed the O twald vess l is equal to

$$\frac{\frac{P}{P-p}\ \frac{73}{273+t}\left\{\Sigma(b)\ \ \Sigma(b\ )\right\} - \frac{273}{293}W}{A}$$

where b and b' are the burette readings before and after intro

ducing the gas into the absorption vessel and W is the volu of solution run out from the absorption vessel

Nature and Magnitude of Errors

In all the experiments an accuracy of 1 in 1000 was aimed at and the values of α given may be taken as correct to 1 in 500 Since the measured volume difference between the first and last readings was always about 100 c c an error of 0 1 c c involves an error of 1 in 1000 in the value of α By far the most important sources of error were (1) inexact levelling when reading the volume of gas in the burette and (2) variations in the temperature of the thermostat

There was no difficulty in reading the burette with a maximum error of 0 05 c c but the exact adjustment of the levelling tube was not so easy In the initial reading when the volume of gas in the apparatus is about 225 c c an error of 1 mm in the levelling involves an error of about 0 33 c c In the final reading when the volume of gas is only half as great a similar error in levelling involves an error of 0 17 c c The actual uncertainty of levelling was probably about a quarter of a millimetre and if the errors in the two readings were additive this involves an error of 1 2 in 1000 in the value of α Thus the probable error introduced by this inaccuracy is 0 6 in 1000

Variations in temperature affect the results in two ways Thus if the temperature of the thermostat is not exactly 20° not only is the volume of gas soluble in the liquid changed by expansion or contraction but the absorption coefficient is also directly influenced Supposing that at the initial reading the true temperature in the thermostat is $(20-\theta)^\circ$ and at the final reading it is $(20+\theta)^\circ$ it can be calculated that the difference between the true and the apparent volume of gas absorbed is

$$\beta + \frac{27300\theta}{293^2+293\theta} + \frac{60060\theta}{293^2-\theta^2} \text{ c c}$$

where β is the difference between the volume of gas soluble in the liquid at 20° and the volume soluble at $(20+\theta)^\circ$ This expression after neglecting θ and θ in the denominator and evaluation of β from the temperature coefficient of solubility of carbon dioxide in water is equal to about 4θ c c Now the maximum variation (2θ) in the temperature of the thermostat was 0 04° and the maximum error from this cause is therefore 0 08 c c that is about 0 8 in 1000

Compared with the above the other errors are unimportant The barometer was read with an accuracy of 0 1 mm and the height of the mercury column was corrected for expansion from

0 to the room temperature The t me interval betwe n the in t al and final read ngs was usually about half an hour and no sensible error was introduced through employing the mean of the two barometer readings since these never diffe ed by more than 0 2 mm and could not as a rule be dete ted Similarly the room temperature was always suffi ently constant during an experiment to preclude the introduction of any appreciable error through employ ng the mean temperature f r the cal ulations There is no doubt that the gas in the absorption ve sel was completely aturated w th water vapour at the second reading on ac ount of the vigorous shaking which always took place or that the gas in the bu ette w s dry sin e the burette tap was always l sed while the ab orption vessel was be ng shaken and gas was never allowed to pa s from the l tter into the bu ette As already stated two determinations were made in e e y case in whi h the a erage difference is 1 7 in 1000 and consequ ntly the probable accuracy of the results is about 1 in 1000

Results

Abs pt c ffi t n II *te* —Four d terminations were n ade and the values fou nd were (i) 0 8775 (ii) 0 8766 (iii) 0 8755 (iv) 0 8766 mean 0 877

This value is in good agreement w th that gi en by Bohr (*W ed Ann len* 1899 **68** 503) namely $_0$ =0 878

T ble I g s the absorpt n c effi ients (α) in the solutions of sucrose exam ned and the sp c fi g av ties of the solut ons at 0

TABLE I

C trat		M	Sp
N/8	0 846 0 8449	0 846	1 01518
N/4	0 8161 0 8140	0 815	1 031 5
N/2	0 7554 0 7563	0 7 6	1 063
N	0 6491 0 6496	0 649	1 12809

In table II a e given the ab o ption coefficients in semi n mal solut ons of the other substances ex mined and for purpo es of reference the pe ific gra t e of the s lutions at 20 and the sp fic g av t s of the solid sub tances at the same temperat re

TABLE II

Substance		Mean a	Sp gr N/2 solution	Sp gr solid
Dextrose	0 7914 0 7928	0 7929	1 0328	1 56 *
Mannitol	0 7822 0 7811	0 7829	1 03031	1 46
Glycine	0 8425 0 8443	0 843	1 01413	1 61
Pyrogallol	0 8529 0 8545	0 853	1 01718	1 45
Quinol	0 8855 0 8876	0 887	1 00946	1 33
Resorcinol	0 9002 0 9024	0 901	1 009 8	1 27
Catechol	0 8676 0 8692	0 868	1 0107	1 34
Urethane	0 8690 0 8682	0 869	1 0037	0 99
Carbamide	0 8634 0 8640	0 864	1 00715	1 33
Thiocarbamide	0 8604 0 8581	0 8 9	1 00917	1 42
Antipyrine	0 8584 0 8600	0 859	1 01339	1 19
Acetamide	0 8790 0 8785	0 879	1 0005	1 6
Acetic acid	—	0 868	1 0026	—
n Propyl alcohol	—	0 869	0 9939	—

* Redetermined

Discussion of Results

Since any theoretical deductions from the results must depend on the way in which the latter are expressed it is first of all desirable to consider briefly the methods which are usually employed for this purpose In order to compare together a number of different substances with respect to their influence on the solubility of a third substance it is of course only permissible to employ solutions of the same molecular concentration Here the usual difficulty arises with regard to the calculation of molecular concentration (compare Abegg *Zeitsch physikal Chem* 1894 **15** 248) The semi normal solutions used in this investigation all contained half a gram molecule in a litre of the solution and this concentration is in many cases considerably different from that of a solution containing the same weight of substance in 1000 grams of water Except in the case of sucrose no experiments with several different concentrations were carried out but the figures for this substance certainly suggest that the volume-normal is more convenient for our present purpose than the weight-normal method of calculation and also that solutions of semi normal

strength are still sufficiently dilute to permit inferences which may be applied without serious error to very dilute solutions

In table III are given values for the molecular depression of solubility calculated according to the volume-normal and weight-normal methods for solutions of sucrose α and α' denote the absorption coefficients of carbon d oxide in pure water and the solution respectively N is the number of gram molecules of sucrose in 1 litre of solution and N' the number in 1000 grams of water

TABLE III

N	$/N$	$/N$
0 12	0 248	0 241
0 2	0 248	0 234
0	0 24	0 216
1 0	0 228	0 180

It will be s en f o ı these figures that the molecular depression alculated by the vol me normal method is con tant for solutions up to $N/4$ and is very little d fferent for those of $N/2$ concentra tion and s nce sucrose produces a much greater effe t than any of the othe substan es examined the de at ns in the case of these mu t be st ll sm ll The purely empirical fo mı la $\alpha - \alpha/N^{\frac{2}{3}}$ suggested by Jahn for expressin the relation between d pression of solubility and concent ation in the case of electro lytes is obviously unsu table for su rose and Roth (*Ze t ch phys l l Che* 189ı **24** 114) has shown that the figures for glyce ol are better repıesented by the l near formula * It is the ef re probably safe to assume th t for moderately dilute solutions of non ele trolytes the effe t on tl e s lub lity of carbon dı xide or of any ınd fferent sl ghtly soluble th rd substan e is d ectly proportional to the amount of non electrolyte present It n w rema ns to cons der certa n atte npts at g ne alısat on In the light of the exper mental data re orded in this pap r

One of the most recent of such attempts s that of Philip (Trans 1907 **91** 711) who suggests that substances which ha e no tendency to combine with the sol ent are without influence on the solubility of an ınd fferent gas whıl t those wh ch do inflıence the solubility do so becau e they remo e a portion of the solvent bv forming compounds w th the latter By solubility is here meant the amount of gas d ssolved by un t m ss of the pure solvent For example the abso ption coefficient of hydrog n in an aqueoı s solution of chloral hydrate s small r than n pure water (Knopp *Z ıtsch pl ysıl l Cl em* 1904 **48** 97) but the amount dissolved

It h ld b m t d th t G ff k (*Z ıts l pl y λ l Che* 1904 **49** 2)
h p t d t uı of tl l t f C d R tl d Pra
wh h y l d t tl pp t pp t tl y fl l t J h p l f m l

by 1000 grams of water is the same in each case This statement is not true however for solutions of sucrose and in order to bring this substance into line it is assumed that the statement would be true if it were not that a certain fraction of the water is withdrawn by the sucrose and the average number of water molecules attached to one molecule of sucrose is calculated in a way consistent with the theory This method of calculation involves three assumptions it presupposes (1) that hydrates are formed (2) that the gas is insoluble in the dissolved substance and (3) that it is insoluble in the hydrate

That such assumptions as these have little foundation in fact may be inferred from the following table which shows the volume of carbon dioxide dissolved by 1000 grams of pure water for the different semi normal solutions examined calculated on the assumption that the water alone is responsible for the absorption of gas observed

TABLE IV

Solution	Carbon dioxide dissolved by 1000 grams of water in c c	Solution	Carbon dioxide dissolved by 1000 grams of water in c c
Water	878	Catechol	908
Sucrose	797	Urethane	907
Dextrose	841	Carbamide	884
Mannitol	833	Thiocarbamide	885
Glycine	864	Antipyrine	935
Pyrogallol	894	Acetamide	906
Quinol	928	Acetic acid	893
Resorcinol	945	i Propyl alcohol	902

It is noticeable in the first place that in eleven out of the fifteen solutions examined a larger quantity of carbon dioxide is dissolved than can be accounted for if the water only is responsible for the absorption This fact alone suffices to show that if we wish to express the solvent properties of these solutions in terms of the properties of their components any conclusions depending on the assumption that the dissolved substance has no solvent power are worthless

It is instructive also to compare from the point of view of the hydrate theory the behaviour of some of these substances with that of the solutions used by Jones and Getman (*Amer Chem J* 1904 **32** 308) in their cryoscopic investigations If the average molecular hydration is calculated in the way described by Philip from the figures given above for sucrose dextrose and mannitol we arrive at the conclusion that sucrose is hydrated to the extent of 3 6 molecules of water dextrose 4 6 molecules and mannitol 5 2 molecules—values which are completely at variance with those deduced by Jones and Getman from their data for the molecular

depression of the freezing point These authors conclude that sucrose in semi normal solution at 0 forms complexes containing about 5 molecules of water whereas dextrose is hydrated only to a small extent and the tendency of mannitol to form hydrates is insignificant It is not intended here to dispute the existence of hydrates in solution but it may be permiss ble to raise the question whether much is to be ga ned by referr ng abnormal depression of solubility to this cause when by so doing it becomes ne essary to make other and more improbable assumptions

Of a d ffe ent haracter is the general ation dedu ed on thermodynamic p n pl s by Jahn (compa e Roth *Z its h phys k l Che n* 1897 **24** 115) Acco di g to this the molecular con centration of a gas remains the same when it is dissol ed to saturation in a dilute solution of an ind fferent non volatile sub stan e as when it satu ates the pure solvent und r the same conditions of temperature and pressure In other words if C_1 denotes the ratio of the numb r of gas molecules to the sum of the molecules of gas and sol ent and C_2 is the rat o of gas molecules to the sum of those of gas s lvent and third substance the theory requires that C_1/C_2 shall be equal to unity prov ded that the follow ng cond t ons a e fulfilled (1) The gas must exert no chem cal a t n on the solvent or the s lution (1) it must ha e the ame mol ular we ght in the l quid as in the gas phase ( ) the solution must be d lute

In a l mited number of cases results ha e b en obta ned which a e des r bed as being in good agreement with the theory Thus Roth (*l c c t*) us ng nit ous ox de found $C /C_2 = 1\ 009$ for ca bamide at about semi normal con entration 1 013 for glycerol and 1 009 for oxalic ac d Braun (*loc c t*) found 1 037 for carbam de and 1 023 for propion c acid in the case of nitrogen and in the case of hydrogen 1 015 for propionic acid Knopp (*l c c t*) found for chloral hydrate when hydrogen was used 0 993 and when n trous oxide was used the ratio was 1 010 for chloral hydrate and 1 037 for propionic acid

Here we ha e values of C_1/C_2 deviating by anything between) 7 and 3 7 per cent from the theoret al value but in view of the fact that the actual change of solubil ty effected lies between the lim ts 1 3 and 4 5 per cent it becomes ob ious that the appa ently good agreement has no significance whatever It should be ment oned that Knopp s experim nts were all ca r ed out at 20 whilst those of Roth and B aun were car ed out at 5 10 15 20 and 25 The figures quoted abo e ref r to the mean of the results obtained at th se fi e temperatures the actual value of C_1/C_2 was found to diminish with rising temperature

In table V the values of C_1/C_2 for the substances employed in the present investigation are tabulated and it is interesting to compare the percentage deviations from the theory given in the third column with the percentage change in solubility of the gas brought about by the non electrolytes used given in the fourth column

TABLE V

Solution	C_1/C	Percentage deviation from $C_1/C_2=1$	Percentage change of solubility
N Sucrose	1 101	10 1	26 0
$N/8$ Sucrose	1 012	1 2	3 5
$N/4$ Sucrose	1 024	2 4	7 1
$N/2$ Sucrose	1 048	4 8	13 8
$N/2$ Dextrose	1 056	5 6	9 [illegible]
$N/2$ Mannitol	1 065	6 5	10 8
$N/2$ Glycine	1 026	2 6	3 9
$N/2$ Pyr[illegible]llol	0 9921	0 8	2 7
$N/2$ Thioc rbamide	1 002	0 2	2 0
$N/2$ Carbamide	1 003	0 3	1 5
$N/2$ Ureth ne	0 9789	2 1	1 0
$N/2$ Antipyrine	0 9494	5 1	2 0
$N/2$ Catechol	0 9762	2 4	1 0
$N/2$ Quinol	0 9554	4 5	1 0
$N/2$ Resorcinol	0 9396	6 1	2 7
$N/2$ Acetamide	0 9795	2 1	0 2
$N/2$ Acetic acid	0 9936	0 6	1 0
$N/2$ n Propyl alcohol	0 9817	1 8	1 0

It will be seen from this table that in no less than seven instances the deviation from the theory actually exceeds the magnitude of the effect which is being studied and in general the extent of the discrepancy increases with the amount of the effect produced There can however be no doubt that the formula deduced by Jahn is inapplicable to the experimental data hitherto available, in other words that the conditions for which the formula is valid are not fulfilled in the experiments Indeed the influence of most non electrolytes is so small that it may reasonably be doubted whether a rigid confirmation of the theory is possible with our present methods of determining gas solubility and in any case there is the possibility that the dissolved substance although chemically indifferent may itself be capable of dissolving the gas employed

An attempt has been made by Roth (*Zeitsch physikal Chem* 1903 **43** 539) to find some common factor which will bring the deviations from Jahn s thermodynamic formula into line with deviations from van t Hoff s freezing point law and it was shown that a parallelism did exist in the cases of glycerol and sucrose both of which give too large a depression of the freezing point and too great a value for C_1/C_2 Thiocarbamide and glycine however give too small depressions whereas the values of C_1/C_2

for these substances are respectively 1 002 and 1 0°6 in semi normal solution at 20 and would of course be greater still at 0

It seems therefore that the effect on the solubility of a gas * produced by non-electrolytes is not capable of explanation by reference either to the formation of hydrates in solution or to deviations from the theory of osmotic pressure—conclusions which have already been expre sed by Levin (*Ze t h physik l Chem* 1906 **55** 513) but that since these effe ts are as Geffcken (*loc c t*) has shown p actically independent of the solub lity of the gas and almost ent rely determined by the nature of the solvent or solution it is only po ble at pres nt to refer them to mutual interaction among the mol cules It only remains to be mentioned that the last-named author has already called attention to a parallel sm wh h exi ts between depressi n or ele at on of solu b l ty and such prop t es as compressibility and surfa e tens n and it is possibl that the whole problem might be more success fully atta ked f m th s point of view

This research was carried out at the suggestion of Prof R thmund to whom I am g eatly ind bted f r much kindly advice and crit c sm as well as for placing at my disposal the necessary apparatus and material

THE INFLUENCE OF RADIUM EMANATION ON EQUILIBRIUM IN A GASEOUS SYSTEM.

FRANCIS LAWRY USHER.

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XLIV.—*The Influence of Radium Emanation on Equilibrium in a Gaseous System.*

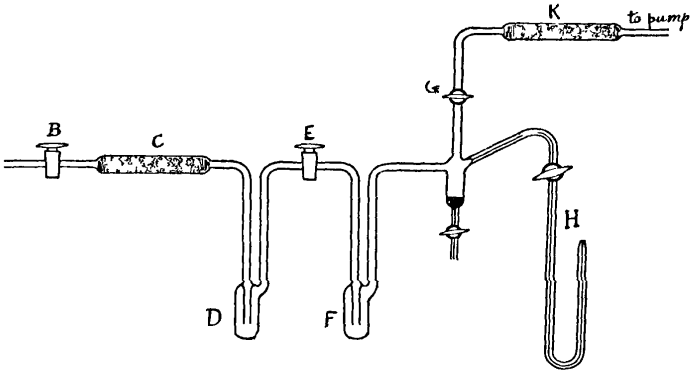
By Francis Lawry Usher.

Some interesting deductions concerning the nature of chemical change induced by radium emanation have lately been recorded by Cameron and Ramsay (Trans. 1908, **93**, 966), as the results of quantitative experiments on the decomposition of water, ammonia, hydrogen

chloride and the oxides of carbor and on the combination hydrogen and oxygen and nitrogen and hydrogen in presence of the emanation

The principal conclusions drawn by these authors are (1) that the changes observed are due almost entirely to the α particles and (2) that each particle of emanation in disintegrating produces *ceteris paribus* the same amount of change The experiments described are regarded by the authors as preliminary and the results have qualitative rather than quantitative significance At the suggestion of Sir William Ramsay, the investigation to be described in this paper was undertaken with the object of obtaining a more definite knowledge of the mechanism of chemical change produced by the emanation

Fig 1



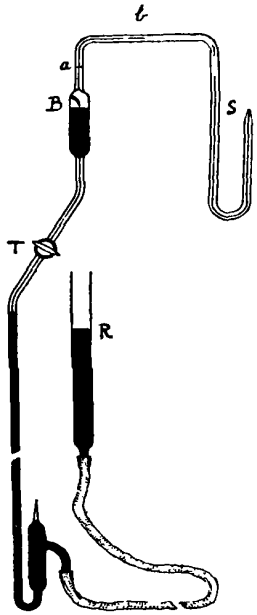
based on an accurate study of the course of some simple reaction For this purpose five series of observations have been made three with pure dry ammonia and two with a mixture of hydrogen and nitrogen of the composition $3H_2+N_2$

Experimental

It will be convenient to describe in detail the method of procedure in the two cases Fig 1 represents the apparatus used for the experiments with ammonia In the first place the tap *B* was closed and the whole apparatus exhausted by means of a small mercury pump Ammonia prepared from pure ammonium chloride and sodium hydroxide, was then introduced through *B* and condensed in the

vessel D which was surrounded w th liquid air B was again closed and the apparatus once more exhausted in o der to remove traces of air The liquid air was removed from D wh ch now contained p i e ammonia, and a convenient quantity of th s (about 1 c c) was p mped off and collected over mercu y in a carefully dried gas tube D was once more cooled with l quid a so as to co den e the ammonia remai ing in the apparatus the tap E was clo ed and the system on the pump side of E thoroughly exhausted Radium emanation accumulated du ing four or five days from a solution contain ing 0 2111 gram of metallic radi m and mixed w th about 0 5 c c of hyd en was no v introduced th ou h the c pillary syphon H and F was then surrounded with liqu d ai After about fifteen minutes in wh ch time all the emanation had condensed the hydrogen was removed through the pump and the required quant ty of ammon a p epa ed in the way desc bed was introd ced throu h H and fro en in F o top of the onden ed emanation If the pump was worked at this stage traces of gas continued to pass over indefinitely and an analysis of the gas thus collected showed it to consist solely of hydrogen and nitrogen so that it appears that solid ammonia is decom posed by the emanation even at -190 The drying tubes C and K contained lime freshly prepared from marble The mixture of ammonia and emanation was next int oduced into the apparatus shown in Fig 2 This cons sted essent ally of a short length (about 5 cm) of gl ss tub ng of 1 cm bore conta n ng an opaque glass point sealed in so as to form a constant-volume gas chamber B the volume contained between a mercury surface set to the po nt an l a mark a on the capillary stem being previously accurately det r mined by calibration with mercury The constant volume chamber terminated above in a capillary syphon S and at its lower end was sealed to a piece of narrower glass tubi g about 80 cms lo g including a stop-cock T the only o e used in the appa at s wh ch was permanently below the mercu y surface and never came into

Fig 2



contact with the gas A mercury reservoir R of the same diameter as the chamber B was connected with the apparatus by a length of rubber pressure tubing The greatest care was taken to dry the inner glass surface thoroughly and for this purpose before the stop cock was greased the entire apparatus was placed in a large air oven and kept at a high temperature for several hours while a current of dried air was passed through it In order to introduce the gas, the apparatus was filled with pure dry mercury and the tube containing the gas was brought over the end of the syphon S in a mercury trough By lowering the reservoir R the gas was admitted and the end of the mercury thread which followed it was set to the mark a on the capillary tubing The thread was then frozen in the horizontal portion of the capillary at b by means of a paper cup containing solid carbon dioxide and the tip of the syphon was then sealed with a small blowpipe flame Finally the apparatus was fixed up against a glass scale ruled in millimetres and frequent readings were taken of the pressure exerted by the gas when the mercury surface was set exactly to the point During the interval between each successive reading the tap T was closed so that the reaction proceeded at constant volume It happened on a few occasions that after the capillary tip had been sealed and the mercury thread had thawed the latter was no longer set exactly to the mark a and in such cases the distance between the two was measured and a correction on the volume was made as the capillary had previously been calibrated by weighing out mercury In making a reading the temperature of the gas and of the mercury column was carefully noted and the barometric height was read at the same time

The above description refers to the experiments with ammonia but those with nitrogen and hydrogen were carried out in exactly the same manner The gases were obtained by sparking pure ammonia over mercury in a glass tube The undecomposed ammonia was removed with a few drops of phosphoric acid the residual mixture of nitrogen and hydrogen was carefully dried and a convenient quantity was collected in a tube in the same way as the ammonia the calcium oxide however being replaced by phosphoric oxide The subsequent procedure differed slightly from that employed in the experiments with ammonia The apparatus shown in Fig 1 was modified to some extent but it will suffice here to say that after thorough exhaustion of the apparatus through the mercury pump the previously dried emanation accompanied by its excess hydrogen was taken in through a capillary syphon the emanation was frozen with liquid air and the hydrogen removed through the pump Finally the liquid air was removed and the sample of nitrogen and hydrogen with

the emanation the mixture being then pumped off and t ansfer ed to one of the reaction vessels already desc ibed

It will be obvious that through ut the wh le of the ope tions just described the e is no pos b lity of se us co t m nati n It is t ue that during the proce s f pur ficat on ga eous e anat n was bro ght into contact with the stop- ocks H G nd E (Fig 1) b t tl e total time of contact between tap grease and emanation was ce ta nly le s than thirty min ites and it w s p oved by a blank exper me t w th emanation and some of the same rubber tap g ease th t if oxygen excluded the only gaseous p oduct f the action is pu e byd g the amount f which produced in half an h ur would be quite negligible

Each expe iment w s ll wed to proceed fo at l st fou week at the end f whi h per od the amount f emanat n st ll p es nt was ins gnific nt D ing the first two d ys read ngs we e take eve y few hours and afterwards at the rate of about one every twe ty fou hours

At the con lus on f each experiment the gas was remov d f om the eacti n ve sel and analysed the ammon a nitroge and hyd og n and gases abs babl by p tas ium hydroxide bei g determi ed Refere c w ll be made to those analyses in the dis ssi n of the results

Experiment I —Volume of react on chamber 2 1187 c c Init al volume of ammon a at 0 and 760 mm = 0 4514 c c About half the quantity of emanat on t ken for this expe ment was accidentally lost so that the propo tion of ammon a to emanation is not known

Tim in d y	C rr ted l f gas	V l m t	$1/t \lg V_0/V$	$1/E \lg V/V$
0 0	0 4514	0 0	—	—
0 56	0 4801	0 029	0 0516	0 0571
0 77	0 4920	0 041	0 0538	0 0620
1 56	0 5183	0 067	0 0448	0 0594
1 83	0 5235	0 072	0 0413	0 0 71
2 58	0 5436	0 09	0 0384	0 0615
4 54	0 5765	0 1 5	0 0301	0 0707
5 54	0 5838	0 132	0 0272	0 074
7 56	0 5956	0 144	0 0 21	0 086
9 67	0 020	0 151	0 0183	0 103
12 58	0 6048	0 153	0 0143	0 137
40 00	0 627	0 176	0 0054	—

Experiment II —Volume of reaction chamber 3 1655 c c Initial volume of ammonia at 0° and 760 mm = 1 843 c c Initial pressure = 474 mm

Time in days	Corrected vol of gas	Volume increment	$1/t \log V/V_t$	$1/E_t \log V/V$
0 0	1 843	0 0	—	—
0 042	1 854	0 011	0 0619	0 0623
0 083	1 871	0 028	0 0801	0 0812
0 104	1 874	0 031	0 0708	0 0720
0 135	1 881	0 038	0 0670	0 068[illegible]
0 191	1 891	0 048	0 0601	0 06[illegible]1
0 865	2 068	0 225	0 0654	0 0764
1 031	2 104	0 261	0 0643	0 0777
1 198	2 145	0 302	0 0649	0 0808
1 854	2 26[illegible]	0 419	0 0605	0 084
2 042	2 302	0 4[illegible]9	0 0610	0 088
2 185	2 323	0 480	0 0600	0 089
2 840	2 416	0 5[illegible]3	0 0 70	0 095
3 230	2 455	0 612	0 0543	0 097
3 840	2 512	0 669	0 0510	0 10[illegible]
3 958	2 523	0 680	0 0505	0 103
5 840	2 652	0 809	0 0430	0 123
6 896	2 703	0 860	0 0396	0 136
7 840	2 724	0 881	0 0360	0 147
8 840	2 757	0 914	0 0337	0 16[illegible]
9 810	2 775	0 932	0 0311	0 183
12 886	2 804	0 961	0 0248	0 253
36 000	2 871	1 028	0 0098	—

Experiment III —Volume of reaction chamber 2 406 c c Initial volume of ammonia at 0° and 760 mm = 0 909 c c Initial pressure = 306 mm

Time in days	Corrected vol of gas	Volume increment	$1/t \log V/V$	$1/E_t \log V/V_t$
0 0	0 909	0 0	—	—
0 031	0 914	0 005	0 0772	0 0776
0 073	0 923	0 014	0 0923	0 0934
0 76	1 037	0 128	0 0868	0 1000
1 08	1 083	0 174	0 0855	0 103
1 75	1 154	0 245	0 0779	0 108
2 08	1 188	0 279	0 0766	0 110
2 78	1 237	0 328	0 0700	0 116
3 75	1 291	0 382	0 0632	0 124
4 75	1 325	0 416	0 0559	0 132
6 75	1 377	0 468	0 0466	0 156
7 76	1 387	0 478	0 0418	0 168
8 75	1 397	0 488	0 0382	0 184
9 75	1 401	0 492	0 0347	0 202
10 76	1 408	0 499	0 0321	0 221
11 76	1 419	0 510	0 0304	0 253
13 77	1 419	0 510	0 0260	0 310
14 76	[1 440]	[0 531]	[0 0258]	[0 359]
15 76	1 419	0 510	0 0227	0 39
32 00	1 433	0 524	0 0117	—

Experiment IV —Nitrogen and hydrogen Same tube as in Exp I Initial volume of mixed gases at 0 and 760 mm = 1 602 c c Initial p essure = 615 mm

T m d y	C rr t d l f gas	V l m m t
0 0	1 602	0 0
0 135	1 585	−0 017
0 698	1 540	−0 062
2 698	1 462	−0 140
2 990	1 460	0 142
3 678	1 442	0 160
4 010	1 441	−0 161
4 698	1 425	−0 177
11 80	1 403	−0 199
31 89	1 362	−0 240

Experiment V —Nitrogen and hyd ogen Same t be in Expt II a t al volume of mixed gases t 0 and 760 mm = 2 323 c c Initial ressure = 594 mm

T m d y	C t d l f gas	V l m n m t
0 0	2 3 3	0 0
0 7	2 273	0 050
1 7	2 247	0 076
2 7	2 230	0 093
4 7	2 241	0 082
5 7	2 228	−0 095
6 7	2 225	0 098
30 0	2 181	0 142

The alysis of the gases at the con lus on of each expe ment w s c d out by means of a sm ll glass b ette pro ded w th a top o k and pillary syphon and cont n ng s x op q e gl ss p ints The volume between a m y su fac s t to ea h of th e points and a ma k on the capill ry stem was accu tely dete m ned by calib ation with me cu y and me s rements we e made by observing ga nst a glass s l the d ffe e ce between the level of the me c y n a ese voir conne ted with the bu ette and th t of the me cu y set exactly to one o other of the points The measu em nts a in all es ect to w th n 0 00 c c The g s w s alw ys mea ed d y and wa f necess y f ex mple afte explosion o t eatment w th wet reagent pumped th ough sm ll tube of phosph ric oxide Ammon w s d termi ed by abso ption with a f w d ps of phos phoric acid hyd gen by expl s n w th me su ed ex s f oxygen and arbon d x de by abso pto w th a lump of fu d a d m ten d potass um hydr xide * The re du l as after emov l f ex e s oxygen by phospho us w s me u ed and con ide ed t be n tro n The t eatment of the gases w th liq d and sol d re gents took place in small gas tubes the g s b ing completely f eed f om the reag nt

A y th d gases des f t g t q tly ll d CO_2

and dried before introduction into the measuring burette Tl following table gives the results of the analyses of the gases at the termination of the experiments

	I	II	III	IV	V
	c c	c c	c c	c c	c c
NH_3	0 173	0 ,8	0 312	0 006	0 010
H_2	0 327	1 56	0 814	0 980	1 321
N	0 121	0 56	0 298	0 356	0 669
CO	0 002	0 014	0 000	0 019	0 185
CO	0 004	0 004	0 009	0 001	0 003

Discussion of Results

It is interesting to compare these results with the figures given by Cameron and Ramsay and for this purpose it is convenient to calculate the values of the expression $Q = 100 \frac{V_\infty - V_t}{V_\infty - V_o}$ and the corresponding logarithms as is done by these authors These values are given in the following table for Expts I and III the reasons for omitting Expts II IV and V will be given pre ently

EXPERIMENT I

Time in days	$V_\infty - V_t$	$Q = 100 \frac{V_\infty - V}{V_\infty - V}$	Log Q	Log $Q/100/t = -k$
0 00	0 176	100 0	2 000	—
0 56	0 147	83 6	1 922	1 392
0 77	0 135	76 8	1 885	1 494
1 56	0 109	62 0	1 792	1 334
1 83	0 104	59 1	1 772	1 245
2 58	0 084	47 7	1 679	1 243
4 54	0 051	29 0	1 462	1 185
5 54	0 044	25 0	1 398	1 086
7 56	0 032	18 2	1 260	0 979
9 67	0 025	14 2	1 152	0 877
12 58	0 023	13 1	1 117	0 702

EXPERIMENT III

Time in days	$V_\infty - V$	$Q = 100 \frac{V_\infty - V}{V_\infty - V}$	Log Q	Log $Q/100/t = -k$
0 00	0 524	100 0	2 000	—
0 76	0 396	75 6	1 878	0 161
1 08	0 350	66 8	1 825	0 162
1 75	0 279	53 3	1 727	0 1.6
2 08	0 245	46 8	1 670	0 159
2 78	0 196	37 4	1 573	0 154
3 75	0 142	27 1	1 433	0 151
4 75	0 108	20 6	1 314	0 144
6 75	0 056	10 7	1 029	0 144
7 76	0 046	8 8	0 944	0 136
8 75	0 036	6 9	0 839	0 133
9 75	0 032	6 1	0 785	0 125
10 76	0 025	4 8	0 681	0 123
11 76	0 014	2 7	0 431	0 133
13 77	0 014	2	0 431	0 114

The figures in the last column of the preced ng tables represent the constant in the eq t on $\frac{V_\infty - V}{V_\infty - V} = e^{-kt}$ or rather the const nt c lculated with common instead of Nap e ian logar thms It will be n ticed that the value of $-k$ d mini hes fa ly egul rly w th time a id that the underlying assumption whi h would requ re t to emain really con tant does n t the efo e st ctly rep ent the fa ts

The t me of half action is in Expt I 2 4 d ys and in Expt III 1 9 days both onsid ably l ss than the half l fe pei od of the emanat on wh h is 3 86 days (S cku) It se m th efo e that the simple hypothesis that each atom of emanati n in de yin p o duces the same amount of change th t n fact the eff ct is at any time proport onal to the amount of eman t n pre ent alth ugh it may be true und ce t cond t on eq ie some mod ficat n to make it a ee w th the exper ments here re ord d

Let us assume that the velocity of eact n at any t me t pr port al both to the amo nt f emanat on and f mm ni p e ent at th t time Then $-\frac{d}{dt} = kE\ k\ V_t = I\ E\ V_t$ Now d ng a ve y mall p ce of t me E consta t s that the above exp e si n can b i teg ted by keeping KE s the co st nt and the r sulting exp ession can be subsequ ntly co rected fo the vari tion of E_t We get then $\frac{1}{t} l\ g \frac{V}{V} = KE$

Fo the sake of comp rison we may consider th t the vel c ty of decompos t on depe d only on the am unt of ammon a p e nt and is not nfluenced by the de y of the emanat on We should then find that $\frac{1}{t} \log \frac{V}{V_t}$ was constant The re ction has been t eat d as an irreversible unimolecular on sin e t s obv ous from the analys s f the g ses at the end f Expts IV and V that rec mb n t n take pl ce t n alm st n ppreciable ext nt Whe eas n E pt III 65 7 pe ent of the mmon a p t in w s decomp ed n Expt IV sta ti g w th n trogen nd hydrog n ly 0 75 per cent of the mixtu e was recombined

The v lues of $\frac{1}{t} l\ g \frac{V}{V}$ nd of $\frac{1}{E\ t} \log \frac{V}{V_t}$ have al e dy b en t b l ted fo Expts I to III on pp 393 394 and it nterest ng to n t that while the const nt be m s malle w th t me wh n no cor e t n fo the d cay of the em nat on s ppl d it b c me l g r wh n the correction is introduced Obv ously t s un e sonable to omit the co re t n for dec y of the em n t on neverth less when the f ll correction is put n the c n tant changes in the opposite d ction although at the me t me a d tinct imp ovement n tice bl It

is here suggested that a third factor namely the *efficiency* of the emanation is required in order to explain the increase of the velocity constant with time Since an α particle is effective over a range of about 8 cm in ammonia gas under the pressures employed in these experiments a large proportion of its energy must be wasted when it is enclosed in a tube of 1 cm bore although this waste need not be proportionately greater at one time than another but one atom of emanation is capable as will be shown later of decomposing at least 134 000 molecules of ammonia It is therefore highly probable than when as in Expt III the emanation is present in the proportion of 1 atom to 10 850 molecules of ammonia the efficiency of an α particle will be greater as its chance of colliding with a larger number of molecules increases, in other words each α particle will do more work when there is more work to do

It is possible to make an approximate correction by assuming that the efficiency is proportional to the ratio of the number of emanation molecules to ammonia molecules at any time although of course this cannot be expected to hold over an extended period

We may assume that $-\frac{dv}{dt} = KE_tV_t\beta_t$ where β_t is the efficiency Then if $\beta_t \propto \frac{V_t}{E_t}$ we get $\frac{1}{V_t t} \log \frac{V}{V_t}$ = constant This expression gives a much better value for K over a period of six or seven days starting at one day from the commencement of the experiment but it afterwards becomes smaller again a result which is to be expected for two reasons first because the assumed correction is the most drastic possible and can only be strictly valid over a very short range and secondly, because a the reaction proceeds the energy of the emanation is more and more used up in useless work namely in imparting increased velocity to the accumulating products of decomposition We can therefore make the further assumption that the efficiency is proportional not only to the ratio of the amounts of emanation and ammonia but also to the actual quantity of ammonia present In this case $\beta_t = \frac{V_t}{E_t} V_t$ and the velocity constant becomes $K = \frac{1}{\sqrt{E_t V_t}\ t} \log \frac{V}{V_t}$ The constants calculated in the two ways suggested are tabulated on p 399 for Expt III

The correction appears to be rather too great in the first case and slightly too small in the second but on the whole both sets of constants are much better than when no correction for change in efficiency is introduced It would doubtless be possible by suitably compromising between the two methods to obtain a still more constant value of K but is it probably not worth while to attempt this because there are

T m d ys.	$K=1/V_t$ l g V_d/V	$K=\frac{1}{\sqrt{t}}$ V_t l g V_d/V
0 073	0 103	0 098
0 76	0 111	0 106
1·08	0 116	0 109
1 75	0 117	0 111
2 08	0 1 1	0 116
2 78	0 120	0 118
3 75	0 1 0	0 121
4 75	0 113	0 1 1
6 5	0 106	0 1 9
7 76	0 097	0 1 7
8 75	0 0 1	0 127
9 75	0 083	0 128
10 76	0 0 8	0 134
11 76	0 0 6	0 138

sl ght compl cations in all the experiments and tl ese will i ow be considered.

It w ll have been not ced in Expt IV th t if the amo nt of n trogen and hyd ogen recomb ned is calcul ted f om the observed ha ge of pressure there should be 0 40 c.c of ammonia at the concl si n of the expe ment. As a m tter of fact the analy i shows that only 0 006 c c was fo med Tl e gases and the app r tus were both ve y caref lly dried the e was no contamination by air and no poss bil ty of leaka e d ring the course of the exper ment the gas was under considerably reduced pressu e the whole time. Clearly then nearly a quarter of a c.c of gas had ceased to ex rt any pressure We can make up a balance sheet with respect to the total quantity f hyd ogen and nitrogen put in at the commencement, and found at the terminat on of two typical e periments Nos. III ar d IV reckoning as hyd ogen and nit ogen these gases in c mbi tion as well as free This bala ce sheet gives the cl e to the observed discrepanc es

	Hydroge p t t mm	N t ge p t t t. co m ce c.c.	Hyd g t f d t d c.c.	N trog f d t d c.
E pt III	1 363	0 454	1 282	0 454
IV	1 201	0 400	0 989	0 3 9

Hydrog lost in E pt.	III	0 081	c.
N t g	III	0 000	
Hydroge	IV	0 212	
N t g	IV	0 041	

in Expt. III a small quantity of n t o en was probably lost for the first re d ng was mad as soon as poss ble after but not at pre i ely the same moment as the emanati n was mi ed w th the ammonia The initial volume ther f e refers to a mixtu e of ammonia with a trace of it decompo ition product and not to pure ammonia as is assumed for the p rpose of the above calculation

In Expt IV we find as one would expect that a larger proportion of hydrogen and nitrogen is missing because the partial pressure of these gases is considerably higher than in the preceding experiment in which no free hydrogen or nitrogen was introduced initially Now this missing gas can only have disappeared in three ways (1) it may have reacted chemically with the glass of which the apparatus was made (2) it may have been driven into the walls of the vessel and remained there or (3) it may have gone completely through the glass The first possibility is very unlikely because nitrogen was lost as well as hydrogen and the glass did not present the appearance of having been attacked only the usual brownish violet coloration was observed

In order to settle this question definitely it was decided to carry out a blank experiment with pure hydrogen and emanation arranged so that any loss of gas could be observed and measured and so as to detect any gas which might pass right through the glass In the meantime the three reaction chambers employed in the five experiments already described were coarsely powdered placed in a piece of Jena glass tubing first exhausted cold by a Topler pump and finally heated to redness and again exhausted nearly 2 c c of gas were pumped out of the heated glass and its composition was as follows The measured total volume was 1 817 c c

CO_2	1 416 c c
CO	0 240
H_2	0 096
N_2	0 066
Total	1 818 c c

The experiment was rather unsatisfactory as the powdered glass was not treated with chromic acid to remove traces of grease dust etc before being heated nevertheless nearly 0 1 c c of hydrogen was recovered and a rather smaller quantity of nitrogen

The apparatus used for the blank experiment was made of glass of about the same thickness as that used in the previous experiments It is diagramatically sketched in Fig 3 The constant volume chamber *C* containing an opaque glass point was itself sealed into a wider piece of glass tubing *A* which was drawn out at the top and connected through a small phosphoric oxide tube with a Topler pump no taps being used The space between the reaction chamber and this outer tube was at the commencement of the experiment very thoroughly evacuated and the pump with which it was connected was worked from time to time during the experiment in order to collect any gas which might be driven through from the reaction chamber

Experiment IV —Nitrogen and hydrogen. Same tube as in Exp I Initial volume of mixed gases at 0° and 760 mm = 1 602 c c Initial pressure = 615 mm :

Time in days.	Corrected vol of gases	Volume increment
0 0	1 602	0 0
0 135	1 585	− 0 017
0 698	1 540	− 0 062
2 698	1 462	− 0 140
2 990	1 460	− 0 142
3 678	1 442	− 0 160
4 010	1 441	− 0 161
4 698	1 425	− 0 177
11 80	1 403	− 0 199
31 89	1 362	− 0 240

Experiment V —Nitrogen and hydrogen Same tube as in Expt II. Initial volume of mixed gases at 0° and 760 mm. = 2 323 c c Initial pressure = 594 mm

Time in days	Corrected vol of gases	Volume increment.
0 0	2 323	0 0
0 7	2 273	− 0 050
1 7	2 247	− 0 076
2 7	2 230	− 0 093
4 7	2 241	0 082
5 7	2 228	− 0 095
6 7	2 225	− 0 098
30 0	2 181	− 0 142

The analysis of the gases at the conclusion of each experiment was carried out by means of a small glass burette, provided with a stopcock and capillary syphon, and containing six opaque glass points The volume between a mercury surface set to each of these points and a mark on the capillary stem was accurately determined by calibration with mercury, and measurements were made by observing, against a glass scale, the difference between the level of the mercury in a reservoir connected with the burette and that of the mercury set exactly to one or other of the points The measurements are in all cases correct to within 0 002 c c The gas was always measured dry, and was, if necessary, for example, after explosion or treatment with a wet reagent, pumped through a small tube of phosphoric oxide. Ammonia was determined by absorption with a few drops of phosphoric acid, hydrogen by explosion with a measured excess of oxygen, and carbon dioxide by absorption with a lump of fused and moistened potassium hydroxide * The residual gas, after removal of excess oxygen by phosphorus, was measured and considered to be nitrogen. The treatment of the gases with liquid and solid reagents took place in small gas tubes, the gas being completely freed from the reagent

Any other acid gases, oxides of nitrogen, etc , are consequently called "CO_2"

removed and re measured in a constant volume point burette already calibrated

Throughout this experiment no gas passed through the walls of the reaction chamber into the surrounding vacuous space which remained quite empty The amount of hydrogen in the tube decreased however, from 0 610 c c to 0 487 c c The following table gives the readings

Time in days	Corrected vol of hydro en	Volume decrease	$k = 1/E\ t \log V/V_t$
0 00	0 573	—	—
1 15	0 530	0 043	0 0363
1 81	0 514	0 059	0 0355
2 81	0 507	0 066	0 0315
3 81	0 10	0 063	0 0261
4 81	0 505	0 068	0 0270
6 81	0 495	0 0 8	0 0313
8 81	0 494	0 079	0 0360
15 81	0 490	0 083	0 0711
25 81	0 489	0 084	0 267

The results are not sufficiently regular to admit of their application as quantitative corrections to the experiments with ammonia and with nitrogen and hydrogen It is even possible that after some time the glass walls of the containing vessel become so pitted by the bombardment that the surface is appreciably altered and in any case the problem is probably much more complicated than it at first appears

At the conclusion of this last experiment the reaction chamber was powdered and the powder was carefully cleared with hot chromic acid washed dried and put in a clean Jena glass tube and exhausted cold It was then exhausted at a red heat and in this way 0 076 c c of gas was extracted Its composition was

CO_2	0 014 c c
H_2	0 061
Total	0 075

There can therefore be no doubt that hydrogen and to a smaller extent, nitrogen is driven into the glass walls of it containing vessel when mixed with radium emanation The greater part of such gas can be recovered when the glass is strongly heated

In calculating the velocity constants and the values of the expression Q it was stated on p 396 that the reasons for omitting Expts II IV and V would be given later IV and V were of course omitted because the observed pressure changes do not really indicate recombination of nitrogen and hydrogen as has just been shown It will be seen on referring to the analysis of the gas from Expt II that although there is an *apparent* loss of

The figures in the last column of the preceding tables represent the constant in the equation $\frac{V_\infty - V_t}{V_\infty - V_o} = e^{-kt}$, or, rather, the constant calculated with common instead of Napierian logarithms. It will be noticed that the value of $-k$ diminishes fairly regularly with time, and that the underlying assumption, which would require it to remain really constant, does not, therefore, strictly represent the facts.

The time of half action is in Expt. I, 2·4 days, and in Expt. III, 1·9 days, both considerably less than the half-life period of the emanation, which is 3·86 days (Sackur). It seems, therefore, that the simple hypothesis that each atom of emanation in decaying produces the same amount of change, that, in fact, the effect is at any time proportional to the amount of emanation present, although it may be true under certain conditions, requires some modification to make it agree with the experiments here recorded.

Let us assume that the velocity of reaction at any time, t, is proportional, both to the amount of emanation and of ammonia present at that time. Then $-\frac{dv}{dt} = kE_t k' V_t = KE_t V_t$. Now, during a very small space of time, E_t is constant, so that the above expression can be integrated by keeping KE_t as the constant, and the resulting expression can be subsequently corrected for the variation of E_t. We get then : $\frac{1}{t}\log\frac{V_o}{V_t} = KE_t$.

For the sake of comparison, we may consider that the velocity of decomposition depends only on the amount of ammonia present, and is not influenced by the decay of the emanation. We should then find that $\frac{1}{t}.\log\frac{V_o}{V_t}$ was constant. The reaction has been treated as an irreversible unimolecular one, since it is obvious from the analysis of the gases at the end of Expts. IV and V that recombination takes place to an almost inappreciable extent. Whereas in Expt. III, 65·7 per cent. of the ammonia put in was decomposed, in Expt. IV, starting with nitrogen and hydrogen, only 0·75 per cent. of the mixture was recombined.

The values of $\frac{1}{t}\log\frac{V_o}{V_t}$ and of $\frac{1}{E_t t}.\log\frac{V_o}{V_t}$ have already been tabulated for Expts. I to III on pp. 393, 394, and it is interesting to note that while the constant becomes smaller with time when no correction for the decay of the emanation is applied, it becomes larger when the correction is introduced. Obviously, it is unreasonable to omit the correction for decay of the emanation ; nevertheless, when the full correction is put in, the constant changes in the opposite direction, although at the same time a distinct improvement is noticeable. It

of the emanation we can calculate the fraction of the total energy of the emanation which is used in effecting chemical decomposition

It is reasonable to assume that the α particles are mainly responsible for the effects observed and further that their power to decompose ceases when they no longer produce any other physical effect that is when their velocity is reduced to 64 per cent of their average initial velocity of projection

On this hypothesis the total kinetic energy of one atom of emanation available for chemical work will be that of three α particle since the atoms of radium A B and C are projected with less than the critical velocity

Now the total kinetic energy of one α particle is 6×10^{-6} ergs hence the energy available for chemical work $= (6 \times 10^{-6}) \times (0\ 64) =$ about $2\ 5 \times 10^{-6}$ ergs

Therefore one atom of emanation produces about $7\ 5 \times 10^{-6}$ erg available energy Taking the mechanical equivalent of heat as $4\ 182 \times 10^{7}$ ergs per calorie this amounts to

$$\frac{7\ 5 \times 10^{-6}}{4\ 182 \times 10^{7}} = 1\ 8 \times 10^{-13} \text{ calories}$$

Now 134 300 molecules of ammonia (which are decomposed by one atom of emanation) require for complete decomposition about $2\ 02 \times 10^{-15}$ calories hence the chemical efficiency of the α particle in this experiment is

$$\frac{2\ 02 \times 10^{-15}}{1\ 8 \times 10^{-13}} = 1\ 12 \times 10^{-2}$$

or a little more than 1 per cent

As regards its influence on equilibrium in the system ammonia–hydrogen–nitrogen it can only be said that if any definite state of equilibrium were reached under ideal conditions it would be one corresponding with a very high temperature Under ordinary conditions there is no true equilibrium but only a state of rest depending on the proportions of ammonia and emanation surface and possibly other factors as well The emanation cannot be called a catalyst in any sense and the effects produced are probably mechanical or electrical in origin

The principal conclusions arrived at in the course of this investigation may be summarised as follows

(1) Ammonia is decomposed by radium emanation at the ordinary temperature and the decomposition is nearly irreversible

(2) Recombination was not observed to take place to a greater extent than 0 86 per cent

(3) Decomposition of solidified ammonia by solidified emanation proceeds with appreciable velocity at -190

Time in days	$A = 1/t \cdot \log V_\infty/V_t$.	$K = \frac{1}{\sqrt{E_t V_t t}} \cdot \log V_\infty/V_t$.
0 073	0 103	0 098
0 76	0 111	0 106
1 08	0 116	0 109
1 75	0 117	0 111
2 08	0·121	0·116
2 78	0 120	0 118
3 75	0 120	0 121
4 75	0 113	0 121
6·75	0 106	0 129
7·76	0 097	0 127
8 75	0 091	0 127
9 75	0 083	0 128
10 76	0 078	0 134
11 76	0 076	0 138

slight complications in all the experiments, and these will now be considered

It will have been noticed in Expt IV that if the amount of nitrogen and hydrogen recombined is calculated from the observed change of pressure, there should be 0 240 c c of ammonia at the conclusion of the experiment As a matter of fact, the analysis shows that only 0 006 c c was formed The gases and the apparatus were both very carefully dried, there was no contamination by air, and no possibility of leakage during the course of the experiment, the gas was under considerably reduced pressure the whole time Clearly, then, nearly a quarter of a c c. of gas had ceased to exert any pressure We can make up a balance sheet with respect to the total quantity of hydrogen and nitrogen put in at the commencement, and found at the termination, of two typical experiments Nos III and IV, reckoning as hydrogen and nitrogen these gases in combination as well as free This balance sheet gives the clue to the observed discrepancies

	Hydrogen put in at commencement. c c	Nitrogen put in at commencement c c	Hydrogen found at end c c	Nitrogen found at end c c
Expt III	1 363	0 454	1 282	0 454
,, IV	1 201	0 400	0 989	0 359

Hydrogen lost in Expt.	III	. .	0 081 c c.
Nitrogen ,, ,,	III		0 000 ,,
Hydrogen ,, ,,	IV		0 212 ,,
Nitrogen ,, ,,	IV		0 041 ,,

In Expt III a small quantity of nitrogen was probably lost, for the first reading was made as soon as possible after, but not at precisely the same moment as, the emanation was mixed with the ammonia. The initial volume therefore refers to a mixture of ammonia with a trace of its decomposition products, and not to pure ammonia, as is assumed for the purpose of the above calculation

Chemistry Department
University of Glasgow,
4th May, 1910

Sir William Ramsay K C B F R S
University College,
London

Dear Sir,

I beg herewith to make application for the post of Professor of Chemistry in the Central College Bangalore India,

As will be seen from my testimonials I am a graduate in Arts and Science with special distinction" in Chemistry of Glasgow University and a Ph D magna cum laude of Gottingen University Germany

I am a fully certificated Normal-trained teacher, and have had three years experience of day-school teaching and almost three years experience of University teaching During 1904-1905 I demonstrated to about 200 students in Junior Laboratories of this University The following Winter Session I was Lecture-Assistant to Professor Ferguson In the Summer Session of 1906 I demonstrated to the Senior Students in Organic Chemistry under Dr T S Patterson On my return from Germany

hydrogen, there is more nitrogen at the end than there was at the beginning, and the same is true for Expt. V. There was no ordinary leakage during either of these experiments, but the same apparatus was used for each, and this curious result may be explained on the hypothesis that there were bubbles in the glass vessel at its junction with the capillary tubing at its upper end, and that the glass was so thin in the region of these bubbles as to become perforated by the α-particles, and so allowed a slow diffusion of air from without. Unfortunately, the discrepancy was not discovered until after the tubes had been ground up.

Chemical Efficiency of the Emanation.

It has been pointed out that in all the experiments hitherto described, the emanation probably brings about only a fraction of the amount of decomposition which it could effect under more favourable conditions. In Expt. III the total volume of ammonia decomposed was 0·597 c.c., and the emanation which was mixed with it was the product of six days' accumulation, and therefore, according to the recent work of Gray and Ramsay (Trans., 1909, **93**, 1073), 0·000081 c.c. In this experiment, then, the ratio of the volumes of emanation and ammonia was 1 to 7380, or, in other words, each atom of emanation decomposed on the average 7380 molecules of ammonia.

In order to get some idea of the amount of chemical work which could be done by the emanation under favourable conditions, an experiment similar to those described above was carried out on a much larger scale. A large round-bottomed flask of 2 litres capacity was filled with ammonia at about 260 mm. pressure, and mixed with six days' accumulation of emanation. The course of the reaction could not, of course, be followed, but, at the end of a month, the gases were pumped out and the quantity of nitrogen and hydrogen produced was roughly estimated. It was found that 10·9 c.c. of ammonia had been decomposed. This is, in every sense, a minimum value, for no account is taken of the fact that that portion of the emanation which was near the walls of the flask was not entirely used up in decomposing ammonia, and no correction is introduced for gas driven into the glass.

There is, however, no doubt that the conditions of this experiment were extremely favourable as compared with those of the preceding ones, and were probably such as to secure at least 90 per cent. of the maximum amount of decomposition. In this case, one molecule of emanation decomposed 134,300 molecules of ammonia.

If we take this as an approximate measure of the chemical efficiency

(2)

Chemical Department

DEPARTMENT OF
METALLURGICAL CHEMISTRY
University of Glasgow

4 May 1910

Dear Sir William Ramsay

One of the chemical assistants here Dr David Thomson is applying for the Professorship now vacant at Bangalore I do know if there is anyone in view for the post but if there is not I should like to recommend Thomson who is an experienced teacher & very enthusiastic He is a man of good physique & would think be a success in India He took his Ph D with Wallach in Gottingen, & is now assisting Dr Patterson in organic lectures & laboratory teaching I do not know the particulars of the post but I take the liberty of sending you this recommendation in case a man has not been found

(3)

TESTIMONIALS

IN FAVOUR OF

DAVID THOMSON, M A , B Sc (Glasgow) Ph D (Gottingen),

late *R bert D n lds Car g* and *18ɔ1 Exhib t o*
R s a h Schola

SKETCH OF CAREER

1895 98 —Pupil Teacher in Old Cumnock Higher Grade School

1898 1901 —Student Church of Scotland Training College for Teachers and University Glasgow

Position at end of *final* year s training—*5th in First Class*

Graduated *M A* of Glasgow University Sub jects of examination English Latin Education Moral Ph losophy Mathematics Natural Philosophy and Chemistry

April 1901—Octr 1902 —First Assistant Lugar Public School

Parchment Certificate as Teacher

1902 03 —(Winter Session) Final B Sc Classes Glasgow Uni ersity

April 1903—Oct 1904 —Assistant Kennedy Street School Glasgow

1904 06 —Final B Sc Classes Glasgow Uni ersity

Classes attended —

Geology & Mineralogy Geologi al Laboratory
Physical Laboratory
Mathematics (Inter and Ad anced Hons)
Chemistry [Inorganic and Metallurgical (adv)
Organic (adv)
Physical and Radioactivity]
Chemistry Laboratory (Inorganic Organic and Physical)

Distinct ons gained in Final B Sc course —

Won *F rst Class* Certificates and a high place in class in *all* Final B Sc subjects
Demonstratorship in Chemistry (£50 per ann) in 1904 05 and 1905 06

SKETCH OF CAREER *(continued)*

April 1906 —Graduated *B Sc* of Glasgow University with SPECIAL DISTINCTION in Chemistry

Appointed ROBERT DONALDSON RESEARCH SCHOLAR in Chemistry (£64 per annum)

1906 07 — CARNEGIE RESEARCH SCHOLAR in Chemistry (£100 per annum)

Published in conjunction with Dr T S Patterson Lecturer in Organic Chemistry Glasgow University two papers —

Uber das Drehungsvermogen in Losungen Ber *40* 1243 1259 (1907)

The Influence of Solvents on the Rotation of Optic ll) Active Compounds Pa t XI Ethyl T rtrate in liphatic Halogen Derivat ves Journ Chem Soc *93* 355 371 (1908)

1907 09 — 1851 EXHIBITION RESEARCH SCHOLAR IN CHEMISTRY Gottingen Germany (£150 per annum)

July 1909 —Graduated Ph D of Gottingen Uni ers ty— MAGNA CUM LAUDE The is *Beitrage zur Kr ge der Abhang gkeit der Drehungs tensit t optisch aktiver Kohlenstoffverb ndungen von der che n schen Konstitution* adjudged by examining commission to be VALDE LAUDABILE

Subjects of examination and examiners for Ph D —
Chemistry (Wallach)
Physical Chemistry (Tammann)
Physics (Riecke)

From Geheimrat Regierungsrat PROFESSOR DR OTTO WALLACH *Director of the University Chemistry Laboratory Gottingen Germany author of Terpene und Campher etc etc*

UNIVERSITATS LABORATORIUM
GOTTINGEN
29 Juli 1909

HERRN DAVID THOMSON aus Glasgow bescheinige ich gern dass er vom Herbst 1907 bis Herbst 1909 im hiesigen Universitats Laboratorium mit einer wissenschaftlichen Arbeit beschaftigt war welche ihm zu seiner Promotion zum Doktor Phil —*magna cum laude*—gedient hat Wahrend dieser Zeit habe ich Herrn THOMSON als ebenso fleissigen wie gewissenhaften und kenntnissreichen Chemiker kennen gelernt den ich bestens empfehlen kann

PROFESSOR DR O WALLACH

From A M WILLIAMS Esq M A *Rector Clas on Provinc al Tra ning College Du idas Vale Build ngs Clasgow*

I HAVE very great pleasure in putting on record my high opinion of Mr DAVID THOMSON M A B Sc Ph D He as a student of mine from 1898 1901 and was one of a small group of men ho showed unusual promise and in whose ork I took a special interest They were all distinguished by intellectual capacity and soundness of character and I have had the pleasure of seeing e ery one of them pursuing a successful career *Mr Thomson s acade n c record at the universities of Glasgo v and Gott ngen is one of the highest d st nction* and he is now an accomplished chem st His knowledge and training would fit him for either the commercial or the academic world He is familiar with the applications of chemistry to the arts while as a fully trained and experienced teacher he would in a university post support his knowledge of his subject by an exceptional command of the method of presenting it I feel quite sure f om what I kno of him that he would d s charge in the most efficient manner any dut es with which he may be entrusted

A M WILLIAMS M A

From T S PATTERSON Ph D (Heidelberg) D Sc (London)
Lect re in Organ c Ch mistry Uni ersity of Glasgow

ORGANIC CHEMISTRY DEPARTMENT
UNIVERSITY OF GLASGOW
24th March 1910

MR DAVID T IOMSON M A B Sc Ph D has been personally known to me fo the last s x years and I ha e much pleas re in test fying to h s ab l t es and exper nce as a chemist Mr THOMSON rece ved most of h s u iderg ad ate tra n ng in Chemistry nder my d rect super s on and in due co se passed the final B Sc exam nat on in Chem stry w th *sp c al d st t* Ther after he took up research work n Ch m t y also und r my d ect on and n 1906 he was appo nted to a Ca neg e S holarsh p wh ch he held fo one year h s work d ng th s t me supply ng mater al for two publ shed papers In 1907 Mr THOMSON was appo nted t the 1851 Lxl ib t on Scholar sh p and proceed n to Cott gen co t n ed to carry on research wo k there grad at ng as Doctor of Philosophy of that Univers ty some n ne months ago Dr THOMSON ha therefore had a very complete tra ng n Chem stry and h s ca e r as a student has been th ougho t mo t su e sful In add t on Dr THOMSON has had nearly three yea s expe ience of un ers tv teach ng wo k

Dur ng 1904 5 he acted as Demo st ator in the Jun or Laboratory here in the winter of 1905 6 he performed the dut es of Lecture Assistant to Profe sor Ferg son and n the Summer Se sion of 1906 wh lst hold ng the Robert Donalds n Research S holarsh p he demonstrated to the Sen or Chem cal St dents in my laboratory and showed in these v rio s capac t es great energy and ab lity

After h s retu n from G tt ngen he was appo nted by the Co rt to as ist n the Organ c Chem st y Laborato y here and du ing the past W nter Sess on he has had e t s e expe en e n the tea hing of st d nts engaged n x rc ses on Q a t tat e Analys s and O gan c P eparat on wo k He al o d l e ed a course of lectures on P act cal Methods of O gan c Chem try to the s nior st dents H s efforts n th s d rect on have been m ch app ec ated both by the students and by myself

Dr THOMSON may be rel ed pon to throw h mself enthus ast cally into any th ng wh ch he unde take and I feel s re that he is tho o ghly capable of f lfill g the dut s of the pos t on of Ass stant Professor n Chem stry at the Her ot Watt College for wh ch post I have much pleasure n recommending h m

T S PATTERSON

Not
He was one of a short list of four candidates for an Assistant-Professorship in the Heriot Watt College Edinburgh. Hence reference in above testimonial D.S.

From CHARLES E FAWSITT D Sc (Edinburgh & Lond) Ph D (Leipzig) *Professor of Chemistry University of Sydney N S W Australia formerly Lecturer in Metallurgical Chemistry University of Glasgow*

METALLURGICAL CHEMISTRY LABORATORY
GLASGOW UNIVERSITY
27th June 1907

I HAVE very great pleasure in stating my high appreciation of the attainments of Mr DAVID THOMSON M A B Sc I have known him for the last three years at Glasgow Uni ersity where he has acted as Demonstrator and Lecture Assistant and as an original investigator in Chemistry

Mr THOMSON S distinguished university record and the experience he has had as a teacher and investigator speak for themselves but I should like to say that as a colleague of mine on the teaching staff I know him to be possessed of very great tact and sympathy for the work of others which have made him uni ersally popular with staff and students alike

The possessor also of great ability and energy and a persevering and faithful worker who never avoids the diffi culties in his path he has fitted himself for a high post in the educational world in which I wish him every success

CHARLES E FAWSITT D Sc Ph D

SONDERABDRUCK.

BERICHTE

DER

DEUTSCHEN CHEMISCHEN GESELLSCHAFT

JAHRGANG XXXX HEFT 6

173 T S Patterson und David Thomson Über das Drehungsvermogen in Lösungen

BERLIN 1907

From T S PATTERSON, Ph D (Heidelberg), D Sc (London),
Lecturer in Organic Chemistry, University of Glasgow

ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW,
24th March, 1910

MR DAVID THOMSON, M A, B Sc Ph D, has been personally known to me for the last six years and I have much pleasure in testifying to his abilities and experience as a chemist Mr THOMSON received most of his undergraduate training in Chemistry under my direct supervision and in due course passed the final B Sc examination in Chemistry with *special distinction* Thereafter he took up research work in Chemistry, also under my direction, and in 1906 he was appointed to a Carnegie Scholarship which he held for one year, his work during this time supplying material for two published papers In 1907 Mr THOMSON was appointed to the 1851 Exhibition Scholarship and proceeding to Gottingen, continued to carry on research work there, graduating as Doctor of Philosophy of that University some nine months ago Dr THOMSON has therefore, had a very complete training in Chemistry, and his career as a student has been throughout most successful In addition, Dr THOMSON has had nearly three years' experience of university teaching work

During 1904 5 he acted as Demonstrator in the Junior Laboratory here, in the winter of 1905 6 he performed the duties of Lecture-Assistant to Professor Ferguson and in the Summer Session of 1906, whilst holding the Robert Donaldson Research Scholarship, he demonstrated to the Senior Chemical Students in my laboratory, and showed in these various capacities great energy and ability

After his return from Gottingen he was appointed by the Court to assist in the Organic Chemistry Laboratory here, and during the past Winter Session he has had extensive experience in the teaching of students engaged in exercises on Quantitative Analysis and Organic Preparation work He also delivered a course of lectures on Practical Methods of Organic Chemistry to the senior students His efforts in this direction have been much appreciated both by the students and by myself

Dr THOMSON may be relied upon to throw himself enthusiastically into any thing which he undertakes and I feel sure that he is thoroughly capable of fulfilling the duties of the position of Assistant-Professor in Chemistry at the Heriot Watt College, for which post I have much pleasure in recommending him

T S PATTERSON.

Note. Last month I was one of a short list of four candidates for an Assistant-Professorship in the Heriot-Watt College Edinburgh Hence reference in above testimonial. D.T.

zu ube... wie dieser Meister ohne Bedenken Konzentrationen bis zu $p = 20—28$ benutzt und hierbei Molekulargroßen ermittelt Hier versteht aber Walden die Stellung welche Beckmann gegen uber der strittigen Frage einnimmt vollkommen falsch wie schon aus dem Umstande hervorgeht daß Beckmann wenige Seiten weiter ausdrucklich darauf hinweist »wie wichtig es bisweilen sein kann das Molekulargewicht au einer Versuchsreihe durch die Kurven ab zuleiten und sich nicht mit einer einzigen Bestimmung zu begnugen« Aus diesen Worten scheint uns mit vollkommener Deutlichkeit her vorzugehen daß Beckmann einen abnormen Wert selbst wenn er ihn in einer nur 9—10 prozentigen Losung erhalten hat nicht als das wahre Molekulargewicht betrachtet vielmehr akzeptiert er nur mit aller Reserve — und keineswegs ohne Bedenken — Zahlen die sich ihm in weit schwacheren als 20—28 prozentigen Losungen ergaben Er cheint bereit hiernach unsere Stellungnahme als gerechtfertigt so kommt noch hinzu daß uns sogar nicht einmal bekannt ist wie man bei Anwendung ziemlich konzentrierter Losungen uberhaupt das Mole kulargewicht berechnen soll

»Bei dem heutigen Stande unserer Kenntnisse« fährt Walden dann fort »kommen daher die in konzentrierten Losungen gewonnenen Molekulargroßen sehr wohl in Betracht ja sie gewinnen ein erhohtes Interesse gerade gegenwartig wo man der chemischen Seite des Losungsphanomens die verdiente Aufmerksamkeit zuwendet« (S 660) In dem Punkt stimmen wir mit Walden vollkommen uberein daß solche Werte sicherlich besondere Beachtung verdienen nicht aber weil sie wie Walden augenscheinlich annimmt wirkliche Molekular gewichte darstellen sondern aus dem Grunde weil wir zurzeit noch nicht wissen wie wir sie interpretieren sollen

Der wesentlichste Teil der Pattersonschen Kritik bezog sich jedoch auf die Inkonsequenz mit welcher Walden die von ihm ge wonnenen Resultate auslegt So schließt Walden z P aus den be zuglich des Acetylapfelsaure dimethylesters vorliegenden An gaben [1]) daß mit der Zunahme des Molekulargewichts auch eine Zu nahme der Drehung von Solvens zu Solvens verknupft ist Hiernach schien sich dann ohne Schwierigkeit weiter argumentieren zu lassen »Wenn nun ein kausaler Zusammenhang zwischen Assoziation und Rotation besteht so durfte doch erwartet werden, daß in einem Losungsmittel in welchem sich das Molekulargewicht rasch mit der Konzentration andert auch das Drehungsvermogen sich ebenso rasch

[1]) Zt chr f physikal Chem 6 442 [1890]

[2]) Walden diese Berichte 38 388 [1905] Patterson diese Berichte 38 4095 [1905]

bezuglich ihrer Anwendung um so großer Die Beziehung zwischen Molekulargewicht und Drehungsvermogen des Acetyl apfelsaure dimethylesters in Schwefelkohlenstoff auf die wir Bezug genommen haben wird von Walden als eine Bestatigung seiner Ansichten ins Feld gefuhrt Die Tatsache daß die Veranderungen in diesem Fall gerade entgegengesetzter Art sind wie man nach dem Verhalten der aktiven Verbindung in verschiedenen anderen Solvenzien erwarten sollte scheinen fur ihn nicht von Bedeutung zu sein und so gilt ihm das was wir als eine in die Augen fallende Widerlegung ansehen als Beweis einer Theorie die nur dadurch gestutzt werden kann daß man jeden Einzelfall fur sich betrachtet und den »logischen Zusammenhang« zwischen den einzelnen Resultaten sorgfaltig ignoriert

Nachdem er so mit Hilfe sich selbst widersprechender Beweise einen Zusammenhang zwischen Molekulargewicht und Drehung in ziemlich konzentrierten Losungen hergestellt hat findet Walden dann auch eine ahnliche deutlich erkennbare Beziehung in unendlich verdunnten Losungen trotzdem hier (beim Acetyl apfelsaure dimethyl ester) die Zunahme des Molekulargewichts von einer Verminderung des Drehungsvermogens begleitet ist[1])

Losungsmittel	C_6H_6 (ebullio kop)	$CH_3\ COOC_2H_5$	$CH_3\ CO\ CH_3$	$CH_3\ OH$
M unendliche Verdunnung	193	240	285	350
$[\alpha]_D$	—32 5°	—25 1°	—22 5°	—24 7°

Dieses Ergebnis steht in vollkommenem Gegensatz zu dem was in konzentrierteren Losungen gefunden wurde der Umstand daß die gleiche Ursache so ganz verschiedene Wirkungen ausubt wird jedoch von Walden nicht einmal der Erlauterung oder auch nur der Erwahnung fur wert gehalten

Wir mochten die gleichen Zahlen jedoch noch in einem anderen Zusammenhang zitieren Das Verhalten des Acetyl apfelsaure dimethylesters in Schwefelkohlenstoff wird von Walden in zwei ganz verschiedenen Richtungen zur Unterstutzung seiner Ansichten herangezogen erstens weil in konzentrierten Losungen gleichzeitig mit hohem Molekulargewicht ein starkes Drehungsvermogen zu erkennen ist und zweitens weil parallel mit Veranderungen der Konzentration sich auch das scheinbare Molekulargewicht und das Drehungsvermogen sehr rasch andern Man sollte demnach erwarten daß da sich diese Beziehung sowohl in konzentrierten Losungen wie auch bei Veranderungen der Konzentration zu erkennen gibt, sie auch in

[1]) Diese Berichte 39 675, 676 [1906]

SONDERABDRUCK.

BERICHTE
DER
DEUTSCHEN
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173. T. S. Patterson und David Thomson: Über das Drehungsvermogen in Losungen.

BERLIN 1907.

[illegible]

[illegible] Probe [illegible] Versuche [illegible] In bezug auf die Äußerung [illegible] [illegible] abgeleitet worden sind; [illegible]

wendung der osmotischen Methoden nachzuweisen Der Grund f letztere Erscheinung liegt nach Walden darin daß eine verdünnte Losung ein physikalisches Gemisch darstellt wahrend eine konzentrierte Losung ein solches nicht ist warum sich dies so verhalt ist allerdings noch keineswegs klar

Wir wiederholen daß uns die Waldenschen Schlußfolgerungen nicht durch das von ihm beigebrachte experimentelle Material gestutzt erscheinen Die Regelmaßigkeiten die er aufgefunden haben will stehen in offenkundigem Widerspruch zu einander wahrend man von einer Theorie die Anspruch auf irgend welchen Wert erheben will doch berechtigter Weise verlangen darf daß sie wenigstens mit sich selbst im Einklang steht Einen bestimmten Fall — z B da Verhalten des Acetyl apfel saure dimethylesters in Schwefelkohlenstoff — nur solange als Beleg heranzuziehen als er die zu beweisende Theorie stutzt und ihn dann ohne ein Wort der Erklarung bei Seite zu lassen sobald er mit der betreffenden Theorie in Widerspruch gerath ferner aus einer Unmenge von Zahlen einige wenige herauszusuchen die eine gezwungene Übereinstimmung mit einer von vornherein auf Grund ihrer »inneren Wahrscheinlichkeit« vorau gesetzten Beziehung zeigen und dann ohne jeden Beweis die auffallenden Ausnahmen von der ersterwahnten Regelmaßigkeit wiederum einer ihrem Wesen nach unbekannten Ursache zuzuschreiben — dieses Verfahren entspricht etwa der Ableitung zweier Unbekannten aus einer Gleichung bei Anwendung dieser Methode kann man jede beliebige Theorie aus irgend einem gegebenen Zahlenmaterial ableiten

In seiner letzten Mitteilung bringt Walden Zahlenangaben uber Molekulargewichte und Drehungsvermogen in unendlich verdunnten Losungen Bei der Diskussion der von ihm fur die Molekulargewichte erhaltenen Werte lenkt er die Aufmerksamkeit auf die Tatsache daß in einer betrachtlichen Anzahl von Fallen »die Molekulargewichte mit zunehmender Konzentration kleiner werden dann fugt er hinzu »Diese Anomalien verdienen eine eingehende Beachtung und Behandlung [1]) Dem stimmen wir durchaus zu Es ist in der Tat etwas uberraschend daß Walden der sich augenscheinlich nur auf eine einzige Reihe von Bestimmungen stutzt (l c S 667 Nr 28) beispielsweise den Schluß zieht das Molekulargewicht des Acetyl apfelsaure dimethylesters wachse in Methylalkohol von 280 7 (c = 4 14) auf 350 bei unendlicher Verdunnung zumal dieses Resultat doch ganz erheblich abweicht von den Ergebnissen jener klassischen Untersuchungen Beckmanns auf welche er uns weiter oben verwiesen hat

[1]) Diese Berichte 39 668 [1906]

Ethyl Tartrate in Bromoform

The bromoform boiled at 40—47° under a pressure of 10—12 mm (oil bath, 80—90°)

I $p = 7\ 0809$

$t°$	16 0°	20 5°	24 8°	39 8°
$\alpha_D^{t°}$ (160 mm)	0 141	0 295	0 447	0 923
$[\alpha]_D^{t°}$	0 47	0 99	1 51	3 17

II $p = 9\ 9976$ *

$t°$	16 9°	22 6°	38 8°	50 6°	59 1°	76 9°
$\alpha_D^{t°}$ (249 6 mm)	0 540	0 891	1 953	2 633	3 075	3 995
$[\alpha]_D^{t°}$	0 86	1 43	3 18	4 34	5 11	6 76

III. $p = 30{\cdot}915$.

$t°$	14 5°	16 9°	28 9°
$\alpha_D^{t°}$ (160 mm)	2 407	2 741	4 041
$[\alpha]_D^{t°}$	2 42	2 76	4 11

Densities determined :

Solvent		I		II *		III	
$t°$	d	$t°$	d	$t°$	d	$t°$	d
19 07°	2 8924	19 04°	2 62003	12 9°	2 5169	19 25°	2 00405
21 17	2 8869	22 56	2 61179	31 0	2 4751	22 67	1 99788
25 75	2 8750	30 03	2 59402	52 0	2 4270	32 17	1 9808
—	—	—	—	73 0	2 3780	—	—

Ethyl Tartrate in Ethyl Bromide.

The ethyl bromide boiled very steadily at 37 8°

I $p = 4\ 9815$

$t°$		20 1°
$\alpha_D^{t°}$ (170 mm)		− 0 119
$[\alpha]_D^{t°}$		− 0 97

II $p = 10\ 92$

$t°$	17 1°	21 5°	26 8°
$\alpha_D^{t°}$ (170 mm)	− 0 381	− 0 240	− 0 003
$[\alpha]_D^{t°}$	− 1 43	− 0 91	− 0 11

III $p = 30\ 576$

$t°$	19 1°	21 5°
$\alpha_D^{t°}$ (70 mm)	− 0 193	0 066
$[\alpha]_D^{t°}$	0 66	− 0 22

IV. $p = 65\ 282$

$t°$	16 6°	23 5°	24 7°
$\alpha_D^{t°}$ (70 mm)	1 319	1 910	2 003
$[\alpha]_D^{t°}$	2 24	3 27	3 43

V. $p = 2\ 01598$.

Only the density of this solution was examined.

This series of observations was carried out with a different sample of bromoform from that used for the other two series. Unfortunately, by an oversight, its density was not determined, and, therefore, this solution does not appear amongst those for which values of molecular solution volume are given on p 371

Weinsäure diäthylester (M = 206)

L	S	C	Δ	M
	1 In Methylalkohol (K = 8 4)			
64 6	2 0121	3 11	0 131°	199 5
64 5	3 0975	4 80	0 215	189 4
64 3	4 9380	7 67	0 337	191 3
64 2	7 5760	11 80	0 509	197 5
71 1	1 9793	1 80	0 088	171 0
70 9	2 8996	4 09	0 182	188
70 8	4 5310	6 40	0 285	188 7
70 6	7 1078	10 07	0 445	190 0
70 4	10 1196	14 56	0 615	196 2
	2 In Aceton (K = 16 7)			
65 6	0 9996	1 52	0 120	212
65 5	2 1613	3 30	0 291	189 4
65 3	3 4701	5 31	0 466	190 4
65 1	4 8155	7 39	0 645	191 3
65 0	5 7586	8 87	0 770	192 3
64 8	7 9739	12 31	1 050	195 7

In den vorstehenden Tabellen haben wir das Molekulargewicht mit Hulfe der von Walden benutzten Konstanten berechnet obgleich diese nicht immer als die besten erscheinen Das Gewicht des Lo sungsmittel wurde nach den durch das Verdampfen erlittenen Verlusten korrigiert

Aus den mitgeteilten Zahlen ergibt sich daß sich die Verbindun gen bei unseren Bestimmungen vollig normal verhielten Die Werte fur den Acetyl apfelsaure dimethyle ter nehmen in allen Fallen mit wachsender Konzentration langsam zu Beim Weinsaurediathylester in Methylall ohol findet man daß die Werte bei den kleinsten Kon zentrationen beider Reihen eine Differenz aufweisen das Molekular gewicht ist hier in dem einen Fall großer im anderen kleiner als normal Doch muß dies zweifellos auf einen experimentellen Irrtum zuruckgefuhrt werden da die anderen Zahlen sehr gut unter einander ubereinstimmen und praktisch auf einer geraden Linie liegen Das Gleiche gilt fur die bei demselben Ester in Aceton erhaltenen Werte mit Ausnahme de ersten Die einzelnen Versuch ergebnisse stimmen sehr gut mit einander uberein und es ist deshalb absolut kein Grund zu Zweifeln vorhanden daß die e Verbindungen statt in unendlich verdunnten Losungen die von Walden angegebenen hohen Werte zu besitzen in Wirklichkeit monomolekular sind Daß in einigen Fallen das Molekulargewicht kleiner als normal gefunden wurde ist aus schließlich auf die Wahl einer ungenauen Konstante zuruckzufuhren

E er ibt h demnach d ß Wein ure d thyle t ri B nz l) M tl yl lkol ol u d Aceton eb llio kop i cl e i no i ales M lek l r gew i ht be t t ur d daß d e von Wal len) gegebenen Zahl n

	B l	M tl yl lk hol	A t
M (b ll o k p s l)	0	34	6
[ ]D	+ 4 (	+ 11 ?	+ 11 6

d rch d e folge i len u e et e s l

	Be l	M thyl lk l l	A t
M (b ll k p h)	n l	m l	al
[ ]D	+ 6 1)	+ 11 5)	+ 11 6

H e i t g l ngt le o i e t te Be hi g len M l k l r ge i lt i nl Dreh g ve ogen cf t z Ve cl w l

C nu d elbe ti tt b Acetyl pfel re d ethyle ter e ve le a s n e e Re lt te d irch l xtr pol t n lg le t t We te 08 n M tl l lkohol i l 100 n Ac ton die W l le che T lelle e geset t e de

	B l	Metl l lk l l	A t
M (ob ll k p h)	193	3 0 (908)	285 (190)
[ ]I	—3	—94 7	— 2

So e h lte w n e B i ele f r e E le l lo a ande er Stelle) d sk t e t wo l t ve cl l e D l g ve moge je i a h d r W hl l L g ttel be no l Mol k la ge l t n llen S l en

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I A s ll ß l tget ilt B ba l t en ir f i o I te e e i pr fe w e et l e o i be gl l l Mole

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) P tt (J Cl m S 81 113? [190?]) l t da M l k l r- g w ht 904 g f l h l W ld (l B lt 39 67 [1906] 2 0 ɔibt

) D c. B lt 39 67 [1906]

) P tte J Ch 81 1107 [190]

) P tt s J Cl S 9 191 [1901]

) P tt J Cl S 9 18 [1901]

kulargewichtes untersuchten Beispiele Beziehungen zwischen dem molekularen Losungsvolumen und dem Drehungsvermogen mit zufriedenstellender Deutlichkeit erkennen ließen Ungluecklicherweise sind jedoch die von Hrn Walden mitgeteilten Zahlen fur diese Zwecke nicht genugend da die von ihm in bezug auf die Dichte der Losungen angegebenen Werte obwohl sie »auf den luftleeren Raum reduziert« werden [1]) mit wenigen Ausnahmen auf 3 Dezimalen abgerundet sind wahrend sich uber die Dichten der Losungsmittel uberhaupt keine Angaben finden

Wir haben deshalb den Acetyl apfelsaure dimethylester bezuglich seiner Rotation und des molekularen Volumens in homogenem Zustande wie auch in Benzol Chloroform und Methylalkohol bei verschiedenen Temperaturen und Konzentrationen untersucht Die hierbei gefundenen Daten sind in den folgenden Tabellen zusammengestellt

Acetyl apfelsaure dimethylester

t^0	$\alpha_D^{t^0}$ (70 mm)	d	$[\alpha]_D^{t^0}$
12 9°	—18 63°	1 2063	—29 07°
25 8	19 51	1 1910	23 40
31 9	19 74	1 1844	23 81
43 1	20 91	1 1724	24 63
64 1	21 07	1 1499	26 20
79 1	21 45	1 1324	27 06
96 0	22 05	1 1137	28 30
133 2	22 58	1 0725	30 08

Beobachtete Dichten

t^0	d	t^0	d	t^0	d
12 9°	1 2064	43 0	1 1724	74 1°	1 1379
21 4	1 1910	49 5	1 1650	99 6	1 1095
33 45	1 1828	62 45	1 1509	141 0	1 0614

$d_4^{20°} = 1\ 1977$

Durch Interpolation findet man hieraus den Wert $[\alpha]_D^{20°} = -22\ 8°$ Walden gibt —22 3° an während Anschutz und Leitter (Zeitschr fur physikal Chem **16** 493 [1895]) —22 8° beobachteten

[1]) Hierdurch wird eine Korrektion erst der funften Dezimalstelle bedingt (vergl Landolt Das optische Drehungsvermogen, 2 Aufl S 408)

ist; niemals aber zeigt sich dieser Mangel deutlicher, als an der folgenden Stelle: »Die in meinem Vortrage besonders hervorgehobenen Faktoren (bezw. die chemische Valenzwirkung zwischen lösendem und gelöstem Stoff) treten aber nach den Massenwirkungsgesetzen gerade in konzentrierten Lösungen zutage. Je geringer die wirksame Masse des optisch-aktiven Stoffes, um so weniger Abweichungen vom additiven Schema wird die Lösung aufweisen, und wir nähern uns einer physikalischen Mischung.« Dies bedeutet, anstatt mit dem Massenwirkungsgesetz im Einklang zu stehen, eine völlige Umkehrung desselben[1]). Je kleiner die zur Wirkung gelangende Masse der optisch-aktiven Verbindung ist, um so größer muß diejenige der zur Wirkung gelangenden Masse des Lösungsmittels sein, und um so größer wird auch die prozentuale Menge derjenigen aktiven Molekule sein, die sich mit dem Lösungsmittel zu einem leicht dissoziierbaren Komplex vereinigen; da sich nun die spezifische Drehung immer bezieht, oder doch wenigstens theoretisch bezieht, auf die gleiche Anzahl von Molekulen einer gegebenen gelösten Substanz, ohne Rücksicht auf die Konzentration, so wird sich der Einfluß der Komplexbildung am deutlichsten in dem spezifischen Drehungsvermögen zu erkennen geben. Nun ist es aber eine wohlbekannte Tatsache, daß die osmotischen Methoden keine Entscheidung darüber zulassen, ob in verdünnten Lösungen eine Vereinigung des Lösungsmittels mit der gelösten Substanz eingetreten ist oder nicht[2]). Es ist deshalb möglich, daß eine bestimmte Substanz sich tatsächlich mit ihrem Lösungsmittel vereinigt und in verdünnter Lösung dennoch ein normales osmotisches Molekulargewicht zeigt; in einem solchen Fall würde aber, sobald die gelöste Substanz aktiv wäre, wahrscheinlich eine Veränderung ihres Drehungsvermögens eintreten. Wir können demgemäß in verschiedenen Solvenzien normale Molekulargewichte finden, aber das Drehungsvermögen wird von Fall zu Fall ein verschiedenes sein. In Wirklichkeit sind auch zahlreiche Beispiele dieser Art gefunden worden.

verdünnter Lösungen

Walden wendet also seine Ideen nicht richtig an. Behufs Erklärung des veränderten Drehungsvermögens in konzentrierten Lösungen setzt er Vereinigung von Lösungsmittel und gelöstem Stoff voraus, während seine Molekulargewichtsbestimmungen (theoretisch) beweisen, daß keine derartige Verbindung eingetreten ist; andererseits verwirft er in verdünnten Lösungen die Annahme einer Komplexbildung, wo nach dem Gesetz der Massenwirkung das Vorhandensein solcher Komplexe viel wahrscheinlicher ist, und wo man hoffen könnte, sie mit Hilfe des Drehungsvermögens, jedoch nicht bei An-

[1]) Vergl. Nernst, Zeitschr. für physikal. Chem. 11, 346 [1893].
Nernst, Ztschr. f. physikal. Chem. 11, 345 [1893].

Acetylapfelsaure dimethylester in Methylalkohol

p = 3 9644

t^0	$\alpha_D^{t^0}$ (400 mm)	d	$[\alpha]_D^{t^0}$
15 4°	—3 185°	0 8077	—24 86°
18 5	3 218	0 8048	25 22
23	3 263	0 8005	25 71
29 5	3 295	0 7942	26 17
20	—	—	25 [1])

Beobachtete Dichten

18 85°	19 27°	20 94°	23 80°
0 80536	0 80405	0 80247	0 79974

p = 10 337

t^0	$\alpha_D^{t^0}$ (170 mm)	d	$[\alpha]_D^{t^0}$
16 6°	—3 536°	0 8255	—24 37°
22 3	3 584	0 8199	24 87
26 2	3 632	0 8160	25 33
29 3	3 644	0 8130	25 51

Beobachtete Dichten

t^0	20 48°	22 13°	24 35°
d	0 82159	0 82000	0 81785

Man ersieht aus diesen Tabellen daß in allen Fallen der Einfluß einer Steigerung der Temperatur sich in dem Sinne geltend macht daß sich das Drehungsvermogen des Esters erhoht Wenn man die so gewonnenen Werte zu einem Diagramm vereinigt wird eine interessante Regelmaßigkeit ganz augenfallig Das Drehungsvermogen nimmt mit dem Ansteigen der Temperatur in Chloroform am schnellsten und in Benzol am langsamsten zu wahrend der Methylalkohol in dieser Hinsicht in der Mitte steht Der Temperaturkoeffizient ist deshalb sehr angenahert proportional dem Werte der Drehung bei 20° Chloroform in welchem man den niedrigsten Wert fur die Rotation findet, hat den großten Temperaturkoeffizienten wahrend Benzol mit dem hochsten Drehungsvermogen den kleinsten Koeffizienten aufweist Das Drehungsvermogen laßt in Uberenstimmung hiermit die Tendenz erkennen bei hoherer Temperatur in allen drei Solventien uberenstimmende Werte anzunehmen Bezuglich dieser Eigenschaft fallt der homogene Ester nahezu in eine Linie mit seinen Losungen sein Drehungsvermogen ist fast eben so groß wie das der methylalkoholischen Losung und auch der Temperaturkoeffizient stimmt

[1]) Interpoliert

Wir haben deshalb eine Reihe ebullioskopischer Bestimmungen angestellt, wobei wir zwei Fälle auswählten, in welchen auf Grund der von Walden mitgeteilten Zahlen ein abnormes Verhalten vorliegt: Äthyltartrat in Methylalkohol und Aceton, sowie Acetyl-äpfelsäure-dimethylester in den gleichen Solvenzien. Unser Apparat war erheblich größer als der allgemein angewendete; er enthielt ungefähr 100 ccm Flüssigkeit. Hierdurch wurde, wie zu erwarten war, erstens leichter ein konstanter Siedepunkt der Flüssigkeit erzielt und zweitens der durch das Verdampfen des Lösungsmittels bedingte Fehler auf ein Minimum reduziert. Das Heizen des Apparates wurde auf elektrischem Wege ausgeführt. Die Konstanz der einzelnen Resultate und ihre Übereinstimmung mit den Beckmannschen Zahlen bringen den Beweis, daß dieses Verfahren verläßlich ist.

Molekulargewichtsbestimmungen
Acetyl-äpfelsäure-dimethylester[1]) (M = 204)

L	s	c	Δ	M
	1. In Methylalkohol (k = 8.4)			
42.6	0.8412	1.97	0.080°	207.4
42.4	1.8040	4.26	0.172	208.0
42.1	4.6520	11.04	0.438	211.8
41.9	7.7421	18.48	0.700	221.7
48.4	1.3359	2.76	0.110	210.7
48.2	2.2050	4.70	0.187	211.3
47.9	4.2780	8.93	0.347	216.1
47.7	6.4681	13.57	0.507	224.8
46.5	0.5825	1.25	0.050	210.3
46.4	1.3643	2.94	0.108	228.9
46.2	2.4514	5.31	0.203	219.6
46.0	4.2720	9.28	0.356	219.0
45.8	7.1787	15.65	0.592	222.1
	2. In Aceton (k = 16.7)			
64.7	0.8184	1.27	0.111	190.4
64.4	2.2302	3.46	0.303	190.9
64.1	3.9452	6.15	0.541	189.8
63.8	5.7690	9.04	0.784	192.5
63.5	7.6919	12.10	1.033	195.7

[1]) So oft wir nach beendigter Molekulargewichtsbestimmung den Ester durch Destillieren zurückgewannen, beobachteten wir, daß dicht bevor der Ester siedete, kleine Mengen eines farblosen, festen Körpers übergingen. Durch Vereinigen des bei verschiedenen solchen Destillationen gewonnenen Materials und Umkrystallisieren aus Aceton konnten wir feststellen, daß die fragliche Substanz bei 94° schmilzt; zu einer weiteren Untersuchung reichte jedoch die allzu geringe Menge nicht aus.

[2]) C = Gramme Substanz in 100 g Lösungsmittel.

stimmung mit der Erfahrung bemerkt man dann auch daß die Verminderung des molekularen Lösungsvolumens in Chloroform mit zunehmender Verdünnung weit rascher vorschreitet als in Methylalkohol. In ersterem Fall verursacht eine Veränderung der Konzentration um 5.51 Einheiten eine Änderung im molekularen Lösungsvolumen um 1.9 ccm, während in Methylalkohol eine Veränderung um 6.38 Einheiten in der Konzentration nur von einer Änderung des Volumens um 0.7 ccm begleitet ist. Beim Übertragen der betreffenden Werte in ein Diagramm ergibt sich dann auch die Möglichkeit, daß in unendlich verdünnten Lösungen das molekulare Lösungsvolumen in Chloroform tatsächlich kleiner wird als in Methylalkohol. Dieses Verhalten wurde mit dem des Äthyltartrats in Chloroform in Einklang stehen[1]; in diesem Fall (das molekulare Lösungsvolumen nimmt hier mit der Verdünnung zu) vollzieht sich die Veränderung in verdünnter Lösung außerst rasch. Eine nur rohe Berechnung ergibt 163 ccm für das molekulare Lösungsvolumen des Acetylapfelsäure-dimethylesters bei unendlicher Verdünnung in Chloroform und 165 ccm für Methylalkohol. Falls diese Werte korrekt sind, so tritt eine deutliche Übereinstimmung zwischen Drehungsvermögen und molekularem Lösungsvolumen zutage:

	Mol. Lsg. Vol. °/₀	$[\alpha]_D^{20°}$
$CHCl_3$	163 ccm	—16.5°
CH_3OH	165	—26°
C_6H_6	172	—33°

Auf dieses Resultat möchten wir jedoch nicht allzu großen Wert legen. Es kann sein, daß bei einer gründlicheren Prüfung sich ergeben wird, daß die von uns angenommene Beziehung in Wirklichkeit nicht besteht, und daß wir es in obigem Beispiel mit einer von jenen Ausnahmen zu tun haben, die Hr. Walden[2]) in folgenden Worten so kühn voraussagt: »Es sei noch hinzugefügt, daß die Zahl der Ausnahmen (von der Beziehung zwischen Drehungsvermögen und molekularem Lösungsvolumen) um so größer wird, je mannigfaltiger die Zahl der untersuchten aktiven Stoffe und je verschiedenartiger die benutzten Solvenzien sind.« Diese Prognose scheint uns übrigens darunter etwas zu leiden, daß sie auf jede Theorie ohne Ausnahme anwendbar ist und auch in erster Linie den Zusammenhang zwischen Molekulargewicht und Drehungsvermögen zu betreffen.

Schließlich möchten wir noch mit aller Deutlichkeit feststellen, daß wir die eventuelle Existenz einer Beziehung zwischen Molekular-

[1]) Patterson, Journ. Chem. Soc. 87, 313 [1905].
[2]) Diese Berichte 39, 663 [1906].

Es ergibt sich demnach, daß Weinsäure-diathylester in Benzol[1]), Methylalkohol und Aceton ebullioskopisch ein normales Molekulargewicht besitzt, und daß die von Walden[2]) gegebenen Zahlen:

	Benzol	Methylalkohol	Aceton
M (ebullioskopisch) .	250	342	365
$[\alpha]_D$	+ 4.7°	+ 11.2°	+ 11.6°

durch die folgenden zu ersetzen sind:

	Benzol	Methylalkohol	Aceton
M (ebullioskopisch) .	normal	normal	normal
$[\alpha]_D$ . .	+ 6.1°[3])	+ 11.5°[4])	+ 11.6°

Hiermit gelangt die vorausgesetzte Beziehung zwischen Molekulargewicht und Drehungsvermögen sofort zum Verschwinden.

Genau dasselbe tritt beim Acetyl-äpfelsäure-dimethylester ein, wenn die aus unseren Resultaten durch Extrapolation abgeleiteten Werte 208 in Methylalkohol und 190 in Aceton in die Waldensche Tabelle eingesetzt werden:

	Benzol	Methylalkohol	Aceton
M (ebullioskopisch) .	193	350 (208)	285 (190)
$[\alpha]_D$	—32.5°	—24.7°	—22.2°

So erhalten wir neue Beispiele für eine Erscheinung, die schon an anderer Stelle[5]) diskutiert worden ist: verschiedenes Drehungsvermögen je nach der Wahl des Lösungsmittels, aber normales Molekulargewicht in allen Solvenzien.

Im Anschluß an die mitgeteilten Beobachtungen war es für uns von Interesse zu prüfen, wie weit die von uns bezüglich des Mole-

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[1]) Patterson (Journ. Chem. Soc. **81**, 1132 [1902]) hat das Molekulargewicht zu 204 gefunden, während Walden (diese Berichte **39**, 675 [1906]) 250 angibt.

[2]) Diese Berichte **39**, 675 [1906].

[3]) Patterson, Journ. Chem. Soc. **81**, 1107 [1902].

[4]) Patterson, Journ. Chem. Soc. **79**, 191 [1901].

[5]) Patterson, Journ. Chem. Soc. **79**, 185 [1901].

Acetyl-äpfelsäure-dimethylester in Chloroform
p = 4 03849

t°	$\alpha_D^{t°}$ (170 mm)	d	$[\alpha]_D^{t°}$
10 44°	—1 682°	1 4946	—16 40°
19 58	1 754	1 4770	17 30
24 1	1 832	1 4687	18 17
27 06	1 858	1 4632	18 50
29 2	1 894	1 4590	18 91
20	—	—	17 4 [1])

Beobachtete Dichten

t°	18.53°	19 25°	21 6°	29°
d	1 47898	1 47764	1 47332	1 45956

p = 9 55419

t°	$\alpha_D^{t°}$ (170 mm)	d	$[\alpha]_D^{t°}$
14 3°	—4 206°	1 4668	—17 6 5°
18 3	4 352	1 4597	18 36
22 6	4 497	1 4520	19 07
24 3	4 522	1 4491	19 22
28 5	4 660	1 4415	19 91
20	—	—	18 64 [1])

Beobachtete Dichten

t°	16 8°	20 3°	22 25°	25°	28 2°
d	1 46217	1 45620	1 45272	1 44775	1 4421

Acetyl-apfelsäure dimethylester in Benzol
p = 4 0387

t°	$\alpha_D^{t°}$ (170 mm)	d	$[\alpha]_D^{t°}$
16 5°	—1 942°	0 8908	—31 74°
20 2	1 934	0 8870	31 76
22 7	1 936	0 8843	31 89
27 8	1 920	0 8789	31 82
45 8	1 884	0 8600	31 91
20	—	—	31 80 [1])

Beobachtete Dichten

t°	16 5°	23 6°	27 5°	28 6°	31 57°
d.	0 89083	0 88349	0 87934	0 8782	0 8736

[1]) Interpoliert

in beiden Fällen fast überein. Statt jedoch, wie erwartet werden konnte, größer zu sein, da das Drehungsvermögen kleiner ist, erscheint er in Wirklichkeit ein wenig, aber auch nur ein wenig, kleiner. Ein ähnliches Verhalten ist beim Methyl-dibenzoyl-glycerat [1]), beim Methylbenzolsulfonat und Methyl-β-naphthalinsulfonat [2]), sowie auch beim Äthyltartrat festgestellt worden.

Fassen wir die Zahlen für Drehungsvermögen und molekulares Lösungsvolumen zusammen, so ergibt sich folgende Übersicht:

Acetyl-äpfelsäure-dimethylester.

$$\text{Mol.-Vol.}^{20^0} = \frac{204}{1.1977} = 170.3 \text{ ccm}$$

$$[\alpha]_D^{20} = -22.8^0$$

In Chloroform ($D_4^{20} = 1.48949$.)

p	d	Mol. Lsg.-Vol. $^{20^0}$	$[\alpha]_D^{20}$
4.03849	1.47626	167.3 ccm	—17.40°
9.55419	1.45672	169.2 »	—18.64°

In Methylalkohol ($D_4^{20} = 0.79203$).

3.9644	0.80336	165.7 ccm	—22.50°
10.337	0.82206	166.4 »	—24.75°

In Benzol ($D_4^{20} = 0.87784$).

4.0387	0.88722	171.6 ccm	—31.8°.

Aus dieser Tabelle läßt sich entnehmen, daß Verdünnung mit Methylalkohol und Benzol die negative spezifische Drehung des Acetyläpfelsäure-dimethylesters verstärkt, wobei das Benzol, wie deutlich zu erkennen ist, die größere Wirkung ausübt. Auf der anderen Seite wird das molekulare Lösungsvolumen in Chloroform und Methylalkohol kleiner, während es in Benzol eine geringe Zunahme aufweist. Die genannten Solventien lassen sich demnach bezüglich der von ihnen hervorgerufenen Rotationswerte in folgende Reihe einordnen:

$$CHCl_3 \rightarrow CH_3.OH \rightarrow C_6H_6;$$

für das molekulare Lösungsvolumen ergibt sich dagegen folgende Anordnung:

$$CH_3.OH \rightarrow CHCl_3 \rightarrow C_6H_6.$$

Diese beiden Reihen stimmen, wie man sieht, nicht mit einander überein. Es muß hierbei jedoch daran erinnert werden, daß eine Beziehung zwischen Drehung und molekularem Lösungsvolumen nur in äußerst verdünnten Lösungen erwartet werden darf; in Überein-

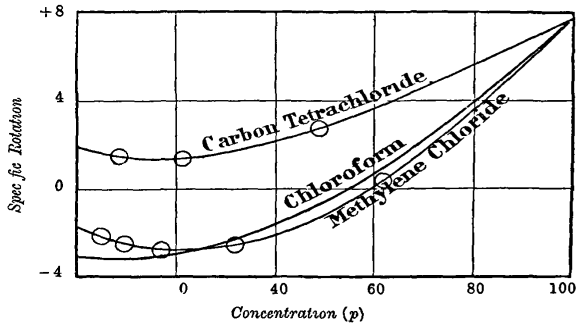
[1]) Frankland, Pickard, Journ. Chem. Soc. 69, 140 [1896].
[2]) Patterson, Frew, Journ. Chem. Soc. 89, 338 [1906].

same relationship as in other cases but in this we were in large measure disappointed although the relationship does hold to some extent Thus in all the solvents under consideration the rotation of the dissolved ethyl tartrate is depressed below that of the homogeneous ester whilst on the other hand the molecular solution volume becomes greater than the molecular volume Amongst the individual data also an inverse proportionality often obtains but a correlation between the two variables cannot be traced through all the solvents examined since exceptions are both numerous and important

It is unnecessary to discuss our results in any great detail the chief points of interest can best be seen from the four accompanying diagrams which summarise the research and in which specific

FIG 1

Ethyl Tartrate in Methylene Chloride Chloroform and Carbon Tetrachloride at 20



rotation is plotted relative to concentration The molecular solution volume curves are not given as they are all of one type and can be just as well represented by numbers as by graphs *

In Fig 1 are shown the concentration rotation curves for methylene chloride chloroform † and carbon tetrachloride The curves are of a similar character but lie perhaps scarcely in the order that might have been expected At a concentration of $p = 30$ the lowest (greatest negative) rotation is found in methylene chloride and the highest in carbon tetrachloride but at great dilution the rotation in methylene chloride lies between the values in the other two solvents This is due

* The experimental data are collected together at the end of the paper The interpolated values for the density of the pure solvents ($p=0$) at 20 /4 and for [ ]^{D} of the various solutions are given with the molecular solution volume data on p 371

† See footnote ( ) p 357

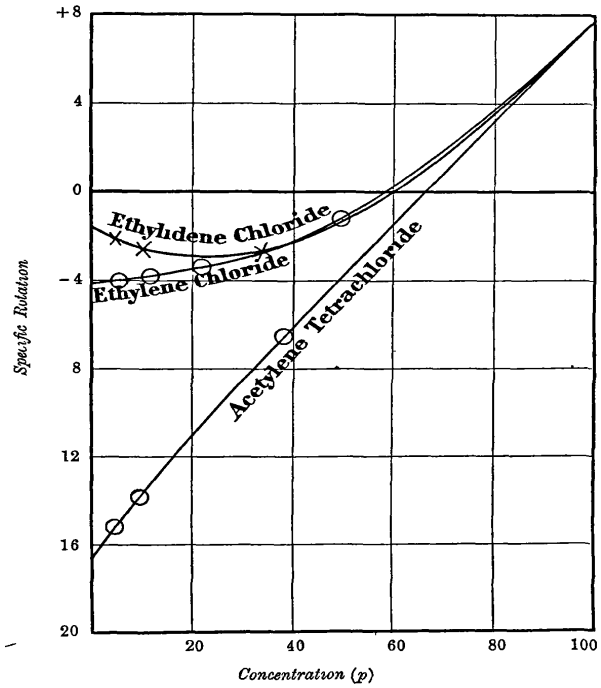
gewicht und Drehungsvermogen gar nicht leugnen wollen. So halten wir es auch fur moglich, daß das Drehungsvermogen von Losungen durch die Bildung instabiler Verbindungen der aktiven Substanz mit dem Lösungsmittel in Mitleidenschaft gezogen werden kann, aber wir vertreten die Auffassung, daß durch die Versuche Waldens bisher weder die eine noch die andere Eventualität bewiesen worden ist. Andererseits sind wir der Meinung, daß in den hierauf hin untersuchten Beispielen der Zusammenhang zwischen molekularem Lösungsvolumen und Drehungsvermogen bei weitem sicherer zu erkennen ist als jede andere Beziehung, die auf diesem Gebiete vermutet worden ist. Hierzu kommt dann noch der weitere Vorteil, daß die Annahme einer Beziehung zwischen Drehungsvermogen und molekularem Losungsvolumen vollig unabhängig von jeder Hypothese sein wurde.

Glasgow, Universitätslaboratorium.

diminishing concentration attaining ultimately to a value of $-16\ 6$ inactivity being already reached in a solution of $p = 66\ 5$ The total depression of rotation (from $+7\ 76$ to $-16\ 6$) is thus more than twice as great as in ethylene chloride It is noticeable also that this curve

FIG 2

Ethyl Tartrate in Ethylidene Chloride Ethylene Chloride and Acetylene Tetra chloride at 20



is concave with reference to the lower right hand corner of the diagram The other curves are convex

The values for the molecular solution volume of ethyl tartrate in these solvents are of considerable interest since in acetylene tetrachloride

he e the rotat on ı so unusually low the vol me should be corre spond ngly g eat

S l t	[ ] (f t d l t)	M S V (fi t d l t)
Ethyl d hl d	1 7	172 8
Ethyl hl d	−4 2	176 0
A tyl t t hl d	−16 6	173 4

It w ll be seen f om the table th t the nve e p opo tıo l ty between the two var ables does occ r n the fi t two solvent The rotatıon ıs lowe and the solut on volume g e ter ın ethyl ne chloride than ın ethyl dene chl de b t ıt s not possıble to reco le the dat f a etylene tet a hlo ıde w th th e fo the other two s lvents the solut on volume does not sh w an ın ease by any means cor espond g wıth the ve y low value of the ot t on

C es epresentıng the behav our of the solvents conta nı g b om ne a e sl own n F g 3 The specific otat on of the ethyl b om de solut o s dım nıshes f ly r p dly w th ınc ea ng d lutıo so as to be ome e o at $p=38$ In solut ns le con entrated than th s the t t n va s mo e sl wly and after $p=10$ the e s p actıcally no change A concentr t on of m n m m rotatıon pe hap occu but f o t s by n mea s d tınct

In b mofo m the ot t on v es less wıth d lut on than n ethyl brom de ne e f ll n below e In dd tıon the cu ve ıs c ncav and thus p e nts a d t nct contrast to the cu ves fo ethyl b m d nd the chl d s B om f m t m y als be n t ced h s a mu l le s p unc d ffect th n chl oform

F om F gs 1 and 2 ıt w ll be se n th t ethylene chlor de ıs sım la to hl of m n ts solvent ınflue ce but s mewhat mo e powe ful In an analogous mann ethyl ne b omıd * g ves a cu ve of the s m type as b omofo m conc ve nd at th s me t me s vastly m p we f l The ınfluence of ethylene b m de becomes g eat as tl e d lut on ıncre ses so that as the concent at o hange f m $p=10$ t $p=0$ the rotatıon f lls f om −10 to −18 8 o one th d f the total ch g

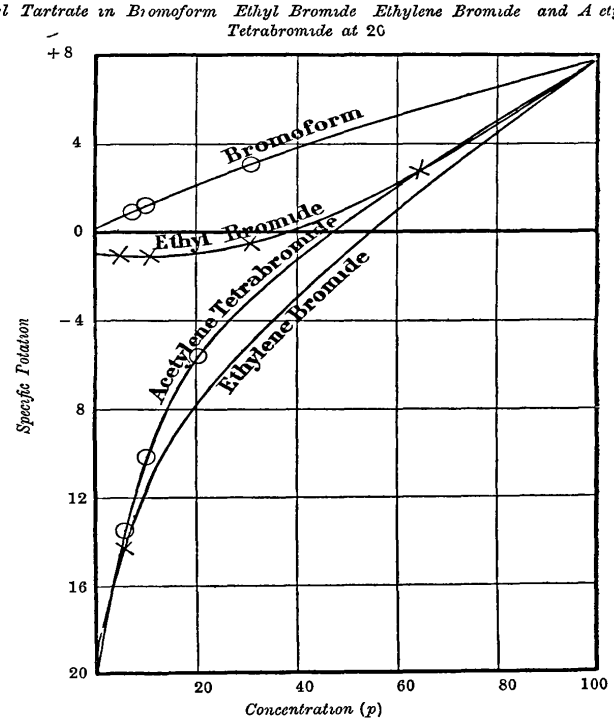
The ınt d t n f t vo mo b om ne at ms ınto the mole ule t to m a tyle e tetrab om de ıs ot ttended by any ve y ma ked alte tıon ın sol ent ınfl ence and ı thus ın d st n t co t t to the behav o r obse ved ın the c s f the co espond g cl l ıles acetyle e tetra hlo de havı g as h ı be n p nt d o t a ve y mu h g eate effect th n ethylen chl de The u v fo acetyl ne tet b om de

Th d t f m h h th u pl tt d th g by W th *B d g t l de ptısh d j g T* Kφb h 1907 p 34 *Z t h phy k l Ch* 1907 **60** 578 Th l t d by p t d by tl d g m O l −14 3 f l t f $p=5$ 59 w ll w th W th l ı f −14 16 f l t f $p=5$ 53

is concave like those for bromoform and ethylene bromide for more concentrated solutions the influence of acetylene tetrabromide is some what less than that of ethylene bromide but in very dilute solut on the effects produced by these two solvents are practically the same

FIG 3

Ethyl Tartrate in Bromoform Ethyl Bromide Ethylene Bromide and Acetylene Tetrabromide at 20



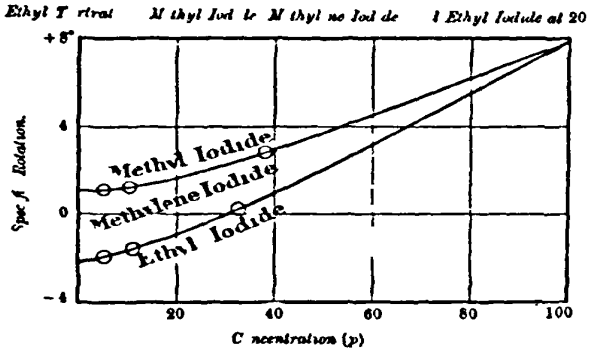
In the table below are given data for solution volume and rotation in these bromides

Solvent	$[\alpha]^{20°}$ (infinite dilution)	M S V $^{20°}$ (infinite dilution)
Bromoform	+0 2	177 0 c c
Ethyl bromide	−0 95	172 6
Ethylene bromide	−18 8	176 7 (p=5 6)
Acetylene tetrabromide	−20 0	176 8

acetylene tetr bromide and etl ylene brou i l in whi h the rota ..ons are very low and almo t equal give soluti n volui es which a e l igh an l almost eq ial wh lst in ethyl bromide a m ich h gher rotati n is accompani d by a con i l rably si aller solution vol ime but it is obv ous that the data f r bromof m are entirely out of harmony with the others tl e rot tion i h gl er than in ethyl bromide whil t tl e lun e is even g e ter th n in acetyl ne tetrabromi l

I F g 4 are shown c rves for the iod d s exami ed M thyl iod le ffects tl e rotation of ethyl tartrate i i s mewhat the same man er and to ch tl e sa e extent as doe ca bon tetrachloride The cur e is of tl.e co ex type l ke those for the chlor des it does not c t

Fi 4



the zero axis and there seems to be no c ce tration of m ni n i i rotat on

The cu ve for ethyl iodide is s m lar to that for methyl iod de b t lies wl lly below it The sub t tuti n of one f the hydrog n atoms in methyl iod de by a n ethyl gro p causes the ef re a greater d pressi g infl ience in th re ulti g as c mpared with tl e oiig al substa ce A s mil r but l ss decided effect was noticed i o p g methylene chlori le and ethyl lene l lo de It n ight pe h i ha e been expected th t tl e greater the proportion of h log n in the sol ent the greater would be the effect produced b t thi i not the case as is shown by the abo e i t ces s well s by se eral others recorded i th s pape

We also attemp t d to u e n eti y l e iodide as a sol ei t b t were surprised to find that ethyl tartrate is o ly ve y slightly s l ble in it, o that we were u able to ex mine more than one mixt re the

specific rotation of which (− 0 8) lay between those for methyl iodide and ethyl iodide

Below are given the molecular solution volume data for these solvents They relate to concentration $p=1\ 4$ since the only solution in methylene iodide was of this strength

Solvent	$[\ ]^{20°}$ ($p=1\ 4$)	M S V ^{20} ($p=1\ 4$)
Methyl iodide	+1 1	179 0 c c
Methylene iodide	− 0 8	177 7
Ethyl iodide	− 2 18	177 8

The solution volume in these three iodides is high in methyl iodide greater than in any other solvent previously examined The values of the rotation however are not by any means in agreement with this being in all three cases in spite of the great density of the solvents comparatively little depressed and standing further in the opposite relationship to solution volume from what was to be expected In methyl iodide where the solution volume is greater the rotation is also greater than in ethyl iodide whilst for methylene iodide and ethyl iodide in which the volume is almost the same the rotation is distinctly different

The method which we have adopted here that namely of dealing with the solvents in classes is probably the most favourable that could be chosen for exhibiting any presumed relationship and yet even in these circumstances exceptions to the suggestion that specific rotation varies inversely with solution volume are numerous and striking and we do not wish to minimise them When the solvents are considered indiscriminately the exceptions become of course more obvious as will be seen from the following table in which all

Solvent	$[\ ]^{20}$ of ethyl tartrate (infinite dilution)	M S V ^{20} of ethyl tartrate (infinite dilution) in c c	N	Diel const ‡	Heat of disgregation §
Carbon tetrachloride	+1 9	173 9	13 3	2 2	41 8
Methyl iodide	+1 08	179 8	—	7 1	41 7
Bromoform	+0 2	177 1	—	4 4	—
Methylene iodide (p=1 4)	*− 0 8*	*177 7*	—	*5 5*	—
Ethyl bromide	− 0 95	172 6	20 7†	(9 7 8 9)	54 7
Ethylidene chloride	− 1 7	172 7	20 8	10 8	60 4
Methylene chloride	− 1 6	174 1	26 87†	—	67 9
Ethyl iodide	− 2 2	178 3	14 8†	7 4	42 5
Chloroform	− 3 0	177 5	18 6	5 0	52 9
Ethylene chloride	− 4 2	176 0	24 6	10 9	73 7
Acetylene tetrachloride	− 16 6	173 6	10 88†	—	—
Acetylene tetrabromide	− 20 0	176 8	—	—	—
Ethylene bromide	− 18 8	176 8	19 6†	4 9	39 3

Schiff *Annalen* 1888 **223** 72 † Calculated according to Schiff s formula

‡ Landolt Bornstein and Meyerhoffer *Tabellen* p 769

§ Calculated from values of heat of vaporisation given in Landolt Bornstein and Meyerhoffer *Tabellen* p 505 See Trans 1901 **79** 195 1902 **81** 1107

to the occurrence in each case of a concentration of minimum rotation, which in chloroform is scarcely perceptible, in carbon tetrachloride is clearer ($p = 20$; $[\alpha]_D^{20°} + 1·35°$), and in methylene chloride is still more distinct ($p = 20$; $[\alpha]_D^{20°} - 2·83°$).

To compare the rotations of these solutions with the molecular solution-volumes, both at infinite dilution, we have the following table :

Solvent.	$[\alpha]_D^{20°}$.	M.S.V.$^{20°}$.
Carbon tetrachloride	$+1·9°$	173·9 c.c.
Methylene chloride.....	$-1·6$	174·1 ,,
Chloroform	$-3·0$*	177·5 ,, †

These numbers stand in inverse order, the lowest rotation corresponding with the greatest solution-volume, and they therefore exhibit the relationship we had expected to find, but it must be admitted that the very small difference between the molecular solution-volume in methylene chloride and carbon tetrachloride seems scarcely sufficient to account for the considerable difference in rotation.

In Fig 2 are shown curves for the other chlorides examined. It will be observed that those for ethylidene chloride and methylene chloride (Fig. 1) are very similar, so that the substitution of one of the hydrogen atoms in the latter compound by a methyl group causes very little change in the solvent influence of the resulting ethylidene chloride. A minimum rotation is somewhat more pronounced in ethylidene chloride ($p = 25$; $[\alpha]_D^{20°} - 3°$), but the value of the rotation at infinite dilution is very nearly the same in both.

On the other hand, a distinct difference is noticeable between the solvent influences of ethylene chloride and ethylidene chloride. From $p = 100$ to $p = 35$, the two curves lie very close together, but at less concentrations they diverge. The rotation in ethylene chloride continues to diminish, and no concentration of minimum rotation is apparent.

The introduction of two chlorine atoms into the molecule of ethylene chloride to form acetylene tetrachloride is attended by a very considerable change in solvent influence. In the latter solvent, the rotation of the dissolved ethyl tartrate diminishes very rapidly with

* Reproduced from Trans., 1905, **87**, 313, where the rotation at infinite dilution was taken as $-3·2°$, the slightly higher value in a solution of $p = 2$ ($[\alpha]_D^{20°} - 3·1°$) as compared with that for a solution of $p = 8·99$ ($[\alpha]_D^{20°} - 3·15°$) being attributed to experimental error. On account of the behaviour of carbon tetrachloride and methylene chloride, however, it is probable that a concentration of minimum rotation exists in chloroform solution, and that the rotation at infinite solution is $-3·0°$ instead of $-3·2°$ as formerly assumed.

† We are of opinion that this value is rather too high.

Ethyl Tartrate in Methylene Chloride

The boiling point of the methylene chloride was not very steady The fraction used distilled between 40 25 and 41 75 at atmospheric pressure

I $p = 5\ 11606$

t	14 1	20 7	24 1	27 0	30 1
α^{D} (160 mm)	−0 308	−0 204	−0 170	−0 116	−0 072
$[\ ]^{D}$	−2 81	−1 88	−1 57	−1 08	−0 67

II $p = 9\ 74502$

t	16 2	20 4	26
α^{D} (160 mm)	−0 638	−0 480	−0 276
$[\ ]^{D}$	−3 08	−2 33	−1 35

III $p = 17\ 0966$

t	16 5	21 3	25 1	29 1
α^{D} (160 mm)	−1 203	−0 929	−0 733	−0 497
$[\ ]$	−3 35	−2 60	−2 06	−1 40

IV $p = 32\ 8988$

t	16 7	21 6	25 5
α^{D} (160 mm)	−2 050	−1 538	−1 090
$[\ ]$	−3 02	−2 27	−1 62

V $p = 61\ 88$

t	19 0	26 9	30 9	32 3	34 7
α^{D} (160 mm)	+0 280	+1 818	+2 588	+2 862	+3 320
$[\ ]^{D}$	+0 23	+1 48	+2 12	+2 35	+2 73

Densities determined

Solvent		I		II	
t	d	t	d	t	d
18 05	1 3397	19 34	1 32865	18 57	1 32249
20 77	1 33467	22 85	1 32246	21 25	1 31792
26 23	1 32464	25 96	1 31693	28 13	1 30607

III		IV		V	
t	d	t	d	t	d
20 37	1 30830	19 5	1 28704	18 86	1 24867
22 11	1 30563	22 88	1 28207	21 42	1 24549
27 20	1 29719	27 33	1 27536	26 45	1 23926

Ethyl Tartrate in Carbon Tetrachloride

The carbon tetrachloride boiled very steadily at 75 75—75 84

I $p = 8\ 82387$

t	18 6	19 5	20 9	25 2	27 9	30 2
α^{D} (160 mm)	0 266	0 324	0 368	0 54	0 612	0 694
$[\ ]$	1 21	1 48	1 68	2 49	2 83	3 22

II $p = 21\ 224$

t	16 1	26 8	31 5	35 8
α^{D} (160 mm)	0 467	1 191	1 509	1 855
$[\ ]^{D}$	0 92	2 37	3 02	3 73

III $p = 48\ 926$

t	16 9	22 3	26 5	30 9	35 3	39 4
α^{D} (100 mm)	1 596	2 014	2 524	2 894	3 170	3 598
$[\ ]^{D}$	2 36	3 00	3 77	4 35	4 78	5 45

where the rotation is so unusually low, the volume should be correspondingly great

Solvent	$[\alpha]_D^{20°}$ (infinite dilution)	M S V ^{20} (infinite dilution)
Ethylidene chloride	$-1\ 7°$	172 8 c c
Ethylene chloride	$-4\ 2$	176 0 ,,
Acetylene tetrachloride	$-16\ 6$	173 4 ,,

It will be seen from the table that the inverse proportionality between the two variables does occur in the first two solvents The rotation is lower and the solution volume greater in ethylene chloride than in ethylidene chloride, but it is not possible to reconcile the data for acetylene tetrachloride with those for the other two solvents, the solution volume does not show an increase by any means corresponding with the very low value of the rotation

Curves representing the behaviour of the solvents containing bromine are shown in Fig 3 The specific rotation of the ethyl bromide solutions diminishes fairly rapidly with increasing dilution, so as to become zero at $p = 38$ In solutions less concentrated than this, the rotation varies more slowly, and after $p = 10$ there is practically no change A concentration of minimum rotation perhaps occurs, but if so, it is by no means distinct

In bromoform, the rotation varies less with dilution than in ethyl bromide, never falling below zero In addition, the curve is concave, and thus presents a distinct contrast to the curves for ethyl bromide and the chlorides Bromoform, it may also be noticed, has a much less pronounced effect than chloroform

From Figs 1 and 2, it will be seen that ethylene chloride is similar to chloroform in its solvent influence, but somewhat more powerful In an analogous manner, ethylene bromide* gives a curve of the same type as bromoform, concave, and at the same time is vastly more powerful The influence of ethylene bromide becomes greater as the dilution increases, so that as the concentration changes from $p = 10$ to $p = 0$ the rotation falls from $-10°$ to $-18\ 8°$, or one third of the total change

The introduction of two more bromine atoms into the molecule to form acetylene tetrabromide is not attended by any very marked alteration in solvent influence, and is thus in distinct contrast to the behaviour observed in the case of the corresponding chlorides, acetylene tetrachloride having, as has been pointed out, a very much greater effect than ethylene chloride The curve for acetylene tetrabromide

* The data from which the curve is plotted are those given by Winther "*Bidrag til den optiske drejnings Teori*," København, 1907, p 34, *Zeitsch physikal Chem* 1907, **60** 578 The one solution examined by us is represented by a cross in the diagram Our value, $-14\ 3°$, for a solution of $p = 5\ 59$ agrees well with Winther's value of $-14\ 16°$ for a solution of $p = 5\ 53$

Ethyl Tartrate in Ethylidene Chloride

The ethylidene chloride boiled very steadily at 57 4—57 5°

I $p = 4\ 64846$

t	11 5	16 1	19 6	22 8	25 3	27 8
α (160 mm)	−0 345	−0 269	−0 195	−0 129	−0 091	+0 057
[ ]$^{\rho}$	−3 9	−3 06	−2 23	−1 48	−1 05	+0 66

II $p = 10\ 6983$

t	11 3	14 0	19 6	21 6
α^{ρ}(160 mm)	−0 906	−0 798	−0 544	−0 452
[ ]	−4 44	−3 93	−2 7	−2 25

III $p = 34\ 237$

12 0	17 0	24 9	27 0
−2 787	−2 215	−1 067	−0 789
−4 29	−3 40	−1 65	−1 22

Densities determined

Solvent		I		II		III	
t	d	t	d	t	d	t	d
17 6	1 17922	19 91	1 17658	19 27	1 17915	19 9	1 1855
21 25	1 17354	23 17	1 17157	22 24	1 17471	25 28	1 17822
29 25	1 16097	27 87	1 16445	28 97	1 16467	27 71	1 17504

Ethyl Tartrate in Acetylene Tetrachloride

The acetylene tetrachloride boiled between 94 and 100° under 15 mm pressure

I $p = 4\ 96198$

t	15 2	21 2	26 9	31 5	36 5
α (160 mm)	−2 075	−1 863	−1 643	−1 453	−1 283
[ ]$^{\rho}$	−16 53	−14 93	−13 24	−11 76	−10 44

II $p = 9\ 314$

	16 0	22 3	29 1	33 4	39 3	48 2	66 4	72 3	92 8	101 3
α^{ρ} (160 mm)—	−3 436	−3 073	−2 617	−2 349	−1 923	−1 533	−0 705	−0 364	+0 202	+0 556
[ ]$^{\rho}$	−14 81	−13 33	−11 42	−10 30	−8 48	−6 82	−3 19	−1 66	+1 17	+2 61

III $p = 38\ 062$

t	15 6	23 1	27 1	30 9	34 6	37 6
α (160 mm)	−6 559	−5 085	−4 253	−3 655	−3 113	−2 415
[ ]	−7 55	−5 90	−4 94	−4 27	−3 65	−2 84

Densities determined

Solvent		I		II		IV	
t	d	t	d	t	d	t	d
18 2	1 60303	18 79	1 57512	21 68	1 54838	17 76	1 42309
21 1	1 5985	22 23	1 56993	31 92	1 53320	23 41	1 41578
26 62	1 58995	27 44	1 56203	32 50	1 5323	28 27	1 40950
29 27	1 5858	—	—	41 0	1 5198	—	—
—	—	—	—	71 2	1 4747	—	—

Densities determined

Solvent		I		II	
t	*d*	*t*	*d*	*t*	*d*
18 32	1 46369	18 7	1 44652	18 95	1 42832
19 62	1 46107	19 77	1 44439	22 9	1 42090
22 5	1 45523	20 93	1 44210	27 20	1 41242

III		IV		V	
t	*d*	*t*	*d*	*t*	*d*
18 85	1 3725	19 57	1 28320	18 47	1 4564
19 37	1 37129	20 17	1 28250	19 07	1 4552
20 10	1 39038	21 20	1 28117	21 6	1 4501

Ethyl Tartrate in Ethylene Bromide

The ethylene bromide boiled very steadily at 34° under a pressure of 14 mm (oil bath 55—58)

$p = 5\ 58716$

t	15 4	18 0	20 7	22 7	42 7	43 4
α (160 mm)	−2 846	−2 762	−2 622	−2 504	−1 734	−1 710
$[\ ]^{t°}$	−15 24	−14 82	−14 11	−13 50	−9 53	−9 41

Densities determined

Solvent		$p = 5\ 58716$	
t	*d*	*t*	*d*
18 1	2 1856	18 02	2 08414
21 37	2 17875	20 18	2 07987
30 55	2 15945	27 82	2 06464

Ethyl Tartrate in Acetylene Tetrabromide

The acetylene tetrabromide boiled steadily at 117° under a pressure of 14 mm (oil bath 155—165)

I $p = 5\ 6676$

t	17 7	20 4	23 0	25 4	44 4
α (160 mm)	−3 46	−3 324	−3 172	−3 014	−2 028
$[\ ]^{t°}$	−13 93	−13 35	−12 85	−12 24	−8 34

II $p = 9\ 9596$

t	16 2	19 6	22 8	31 7
α (160 mm)	−4 53	−4 21	−3 904	−3 146
$[\alpha]^{t°}$	−11 01	−10 26	−9 54	−7 74

the data referred to are brought together The solvents are arranged in order of magnitude of the rotation, and, since in former papers a certain connexion seemed traceable between rotation and surface tension, dielectric constant, and heat of disgregation, we have added values found by various observers for these three properties of the solvents used

It will be seen that there is certainly no greater apparent relationship between the numbers in the last three columns and the values of the rotation than exists between the latter and the data for solution volume

Other suggestions which have been made to account for variation of rotation in solution are even less successful It has been shown already (Trans , 1902, **81**, 1113) that osmotic molecular weight in dilute solution seems to have no connexion with rotation, and a further illustration of this is to be found in the case of ethyl tartrate in ethylene bromide As Winther (*Bidrag til den optiske drejnings Teori*, p 42 , *Zeitsch physikal Chem* , 1907, **60**, 584) has found, the cryoscopic molecular weight in very dilute solution is normal Thus in water, benzene, and ethylene bromide, to take only three examples, the molecular weight of ethyl tartrate is normal, whilst the respective specific rotations are +26 96° (Trans , 1904, **85**, 1130), +6 1° (Trans , 1902, **81**, 1107), and −18 8°

Reference has been made in the previous part of this investigation (Trans , 1907, **91**, 1843) to the possibility of combination of solute and solvent It is clear, so far as our solutions are concerned, that, since we have at present no means of determining the number of molecules of solvent that combine with one molecule of solute—if such combination occurs at all—and, further, no means of determining the value of the equilibrium constant, an attempt to apply this idea would be premature Certainly no indications of combination similar to those observed by Irvine (Trans , 1906, **89**, 1568) or by Gennari (*Zeitsch physikal. Chem* , 1896, **19**, 130 See also Winther, *Bidrag til den optiske drejnings Teori*, p 115 , *Zeitsch physikal Chem* , 1907, **60**, 681) have been met with by us in the course of these experiments

Experimental

The ethyl tartrate used had $\alpha_D^{18\cdot1}$ +9 153° The various solvents (which were obtained from Kahlbaum) were purified by washing with dilute alkali and with water, drying with calcium chloride, and distillation, either at atmospheric pressure with a Young column or under reduced pressure

Densities determined

Solvent		$p=1\ 4233$	
t	d	t	d
19 41	3 32605	21 06	3 23649
21 5	3 32138	22 91	3 23154
26 75	3 3074	26 72	3 22161
29 15	3 3010	33 48	3 2038

Ethyl Tartrate in Ethyl Iodide

The ethyl iodide boiled at 72 25—72 3° under atmospheric pressure

I $p=5\ 17118$

t	20 6	25 2	27 0	50 2
$\alpha_D^{t°}$ (170 mm)	−0 3	−0 194	−0 106	+0 462
$[\ ]^{t°}$	−1 82	−1 19	−0 65	+2 91

II $p=10\ 6333$

t	12 8	19 7	25 4	30 6	45 9
α (170 mm)	−0 824	−0 465	−0 215	+0 033	+0 519
$[\alpha]^{t°}$	−2 51	−1 42	0 66	+0 10	+1 63

III $p=32\ 766$

t	18 7	26 2	29 2	30 6
$\alpha_D^{t°}$ (170 mm)	0 057	1 003	1 389	1 651
$[\ ]_D^{t°}$	0 06	1 13	1 57	1 87

Densities determined

Solvent		I		II		III	
t	d	t	d	t	d	t	d
19 25	1 93875	18 58	1 87591	18 22	1 81533	18 07	1 60740
20 99	1 93483	19 33	1 87422	20 41	1 81067	20 46	1 60373
24 54	1 92654	21 38	1 86976	21 75	1 80801	25 33	1 59553
32 35	1 90862	24 17	1 86367	26 01	1 79910		
		32 9	1 84426				

Molecular Solution Volume and Specific Rotation at 20 of Ethyl Tartrate in Various Solvents

Molecular volume of ethyl tartrate at 20° $= \frac{206}{1\ 2053} = 170\ 91$ c c

For the homogeneous ester, $[\alpha]_D^{20°} = +7\ 76$

Solvent	p	d 20 /4	M S V ^{20} c c	$[\ ]^{20}$
Methylene chloride	0	1 3361	174 1	−1 60
	5 11606	1 32749	173 73	−2 08
	9 74502	1 32006	173 4	−2 40
	17 0966	1 30890	172 92	−2 79
	32 8988	1 2863	172 32	−2 50
	61 8807	1 2473	171 93	+0 36
	Extrapolated			

Molecular Solut on-Volu ıe an l Spec fic Potatıon at 20 *of Etl yl Ta trate ın Va ıous Solvents* (continued)

S l t	*p*	*d* 20 /4	M S V 20°	[20°
C b t t hl d	0	1 59472	173 90	+1 9
	8 8239	1 54858	172 79	+1 53
	21 224	1 49033	171 81	+1 38
	48 926	1 3762	171 11	+2 75
Ethyl hl d	0	1 25350	176 0	4 20
	5 8702	1 24868	175 14	4 07
	11 733	1 24457	174 39	3 80
	22 03 9	1 23833	173 47	3 40
	49 7182	1 22417	172 26	−1 22
Ethyl d hl n l	0	1 17549	172 8	−1 70
	4 64846	1 17644	172 2	−2 15
	10 6983	1 17806	1 1 67	−2 63
	34 237	1 1854	170 97	−2 68
A tyl t t hl d	0	1 6002	173 4	−16 60
	4 96198	1 57330	173 1	−15 20
	9 3140	1 5508	172 8	−13 80
	38 0616	1 4 02	171 6	6 55
B m f m	0	2 8899	177 0	+0 20
	7 0809	2 61778	175 93	0 93
	9 9976†	—	—	1 19
	30 915	2 0027	173 43	3 09
Ethyl b m d	0	1 45983	172 6	−0 95
	2 01598	1 45333	172 41	—
	4 9815	1 44395	172 26	0 98
	0‡	1 46018		
	10 92	1 42631	171 75	−1 05
	30 576	1 370 5	171 25	−0 52
	65 282	1 8272	170 97	+2 73
Ethyl b m d	0	2 1816	—	−18 8
	5 58 16	2 08023	176 78	14 3
A tyl t t b d	0	2 9638	176 8	−20 0
	5 6676	2 72804	175 49	13 47
	9 95956	2 57561	174 69	10 19
	20 1106	2 27798	173 56	5 53
M thyl d d	0	2 27899	179 8	1 08
	5 19605	2 17005	177 77	1 13
	10 4466	2 07288	176 42	1 20
	38 0809	1 68698	173 67	2 85
M thyl d d	0	3 3 537	—	—
	1 4233	3 23921	177 7	0 8
Ethyl d d	0	1 93 06	178 3	2 2
	5 17118	1 8 279	176 9	−1 88
	10 6333	1 8115	175 6	−1 46
	32 766	1 6044	173 6	+0 24

E t l l t d † See t p 367
‡ A f h m l f thyl b m d w d f tl t tl l t

It gives us pleasure ın conclusıon to acknowledge our ındebtedness to the Re earch Fund Committee of the Chemical Society for a grant which def ayed the expenses of thıs ın esti ation

Th Un ty Glas w

Beiträge zur Frage der Abhängigkeit der Drehungsintensität optisch aktiver Kohlenstoffverbindungen von der chemischen Konstitution

(4/3)

Inaugural Dissertation
ur
Erlangung der Doktorwurde
der
hohen philosophischen Fakultat
der
Georg August Universitat zu Gottingen
vo gelegt on

David Thomson
a is Glasgow S hottla d

Göttingen
Druck der D eterich schen Univ Buchdru kerei (W Fr Kaestner)
1909

Tag der mundlichen Prufung 14 Juli 1909
Referent Herr Geh Reg Rat Prof Dr O Wallach

Molecular Solution-Volume and Specific Rotation, at 20°, of Ethyl Tartrate in Various Solvents (continued)

Solvent	p	d 20°/4°	M S V ^{20} c c	$[\alpha]_D^{20°}$
Carbon tetrachloride	0	1 59472	173 90*	+1 9*
	8 8239	1 54858	172 79	+1 53
	21 224	1 49033	171 81	+1 38
	48 926	1 3762	171 11	+2 75
Ethylene chloride	0	1 25350	176 0*	−4 20*
	5 8702	1 24868	175 14	−4 07
	11 733	1 24457	174 39	−3 80
	22·0379	1 23833	173 47	−3 40
	49 7182	1 22417	172 26	−1 22
Ethylidene chloride	0	1 17549	172 8*	−1 70*
	4 64846	1 17644	172 2	−2 15
	10 6983	1 17806	171 67	−2 63
	34 237	1 1854	170 97	−2 68
Acetylene tetrachloride	0	1 60022	173 4*	−16 60*
	4 96198	1 57330	173 1	−15 20
	9 3140	1 5508	172 8	−13 80
	38 0616	1 4202	171 6	−6 55
Bromoform	0	2 8899	177 0*	+0 20*
	7 0809	2 61778	175 93	0 93
	9 9976†	—	—	1 19
	30 915	2 0027	173 43	3 09
Ethyl bromide	0	1 45983	172 6*	−0 95*
	2 01598	1 45333	172 41	—
	4 9815	1 44395	172 26	−0 98
	0‡	1 46018		
	10 92	1 42631	171 75	−1 05
	30 576	1 37055	171 25	−0 52
	65 282	1 28272	170 97	+2 73
Ethylene bromide	0	2 1816	—	−18 8*
	5 58716	2 08023	176 78	−14 3
Acetylene tetrabromide	0	2 9638	176 8*	−20 0*
	5 6676	2 72804	175 49	−13 47
	9 95956	2 57561	174 69	−10 19
	20 1106	2 27798	173 56	−5 53
Methyl iodide	0	2 27899	179 8*	1 08*
	5 19605	2 17005	177 77	1 13
	10 4466	2 07288	176 42	1 20
	38 0809	1 68698	173 67	2 85
Methylene iodide	0	3 32537	—	—
	1 4233	3 23921	177 7	−0 8
Ethyl iodide	0	1 93706	178 3*	−2 2*
	5 17118	1 87279	176 9	−1 88
	10 6333	1 81155	175 6	−1 46
	32 766	1 6044	173 6	+0 24

* Extrapolated † See note on p 367.
‡ A fresh sample of ethyl bromide was used for the next three solutions.

It gives us pleasure, in conclusion, to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant, which defrayed the expenses of this investigation

THE UNIVERSITY, GLASGOW

RICHARD CLAY AND SONS, LIMITED,
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BUNGAY, SUFFOLK.

Theoretischer Teil

A Einleitendes Die van t Hoff Le Belsche Theor im Lichte der neueren Forschungen

Die nachfolgende Arbeit hat zum Zweck Beitrage zur Frage zu liefern in welchem Sinne sich die optische Drehung einer Substanz abhangig von der Konstitution erweist. Als Ausgangskorper sind Verbindungen der Thujonreihe gewahlt worden Bei der Gelegenheit sind auch sonstige Beobachtungen gemacht welche fur diese Verbindungsgruppe nicht ohne Wichtigkeit sind und welche im experimentellen Teile beschrieben werden

Um das was uber die Drehung ermittelt worden ist in ihren eventuellen Beziehungen verstandlich zu machen mochte ich eine kurze Einleitung uber die van t Hoff Le Belsche Theorie der optischen Drehung im Lichte der neueren Forschungen vorausschicken

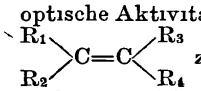
van t Hoff und Le Bel machten bekanntlich die folgenden klaren und einfachen Voraussetzungen

Erstens Die Valenzrichtungen des Kohlenstoff atomes liegen nicht in ein und derselben Ebene sondern sind paarweise auf zwei sich schneidende Ebenen ver teilt

Zweitens Opti ch aktive Verbindungen enthalten ein oder mehrere asymmetrische Kohlenstoffatome d h

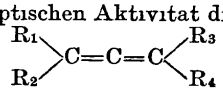
Kohlenstoffatome vom Typus C ($R_1 R_2 R_3 R_4$) wo R_1, R, R_3, R_4 stofflich oder strukturell verschiedene Atome oder Atomgruppen darstellen

van t Hoff stellt sich die Anordnung der Valenzen in der Hauptsache unter dem Bilde eines regularen Tetraeders vor, in dessen Zentrum sich das asymmetrische Kohlenstoffatom befindet Daher ist keine optische Aktivitat bei den Verbindungen des Olefintypus

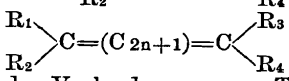


zu erwarten Denn, wenn man ein Modell einer solchen Verbindung aus regularen Tetraedern zusammenstellt, werden immer die vier Gruppen R_1, R_2, R_3, R_4 in einer Ebene liegen, die eine Symmetrieebene ist Hier waren die Ansichten von van t Hoff und Le Bel nicht ganz ubereinstimmend, denn der letztere nahm an, daß optische Aktivitat bei diesem Typus nicht ausgeschlossen ware (s van t Hoff „Lagerung der Atome" II Aufl S 3)

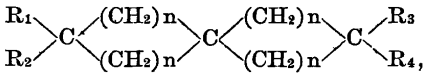
van t Hoff (l c S 75—76) sieht als zweiten Fall der optischen Aktivitat die Verbindungen vom Allylen typus



oder im allgemeinen



voraus Hierunter fallen auch die Verbindungen vom Typus –



da offenbar die gegenseitige Stellung der Endkohlenstoffatome, also auch die der Gruppen R_1, R_2, R_3, R_4 in jedem Falle dieselbe ist Ein Tetraedermodell zeigt in jedem Falle, daß die Gruppen R_1 R_2, R_3, R_4 nicht mehr

in einer Ebene, wie im Olefintypus sondern in Ebenen liegen die auf einander senkrecht stehen

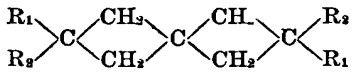
$$\begin{matrix} R \\ R_3 + R_4 \\ R_2 \end{matrix}$$

Eine Verbindung von diesem Typus ist bisher meines Wissens noch nicht dargestellt worden

Die praktische Untersuchung hat im vollem Maße die Richtigkeit der Theorie bewiesen denn wie Landolt (Das optische Drehungsvermogen II Aufl S 46) sagt Es zeigt sich daß ausnahmslos die Aktivitat mit dem Vorhandensein asymmetrischen Kohlenstoffes verbunden ist und daß Korper welchen solcher fehlt niemals Drehungsvermogen besitzen

In den letzten Jahren hat sich aber herausgestellt daß zwei wichtige Falle von van t Hoff ubersehen wurden Ihrer Wichtigkeit wegen sollen sie hier erortert werden

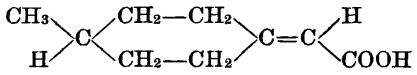
Aschan (Ber 3o 3396 (1902)) scheint zuerst darauf hingewiesen zu haben daß für das Auftreten der optischen Aktivitat bei Verbindungen des Allylentypus es nicht notig ist daß die vier Gruppen R_1 R_2 R_3 R_4 alle verschieden sein mussen sondern daß die Bedingung der Asymmetrie durch den Typus



befriedigt wird indem ein Tetraedermodell einer solchen Verbindung mit seinem Spiegelbilde nicht zur Deckung gebracht werden kann [1])

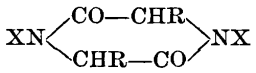
1) D ob ge A y m t e ka n f lge d rmaße kl r ge acht we de Die vier G ppe R R R R stelle d e Lcken e s te tra drische Sphe o ds d E s l hes Sl he oid ka n ko tr ert

Perkin, Pope und Wallach (Proc Chem Soc (1909) 3o4, 83) haben eine solche Verbindung in der 1 Methyl cyklohexyliden 4 essigsaure



dargestellt und sie in ihre aktiven Formen gespalten Hier haben wir also einen Fall von optischer Aktivitat ohne das Vorhandensein eines asymmetrischen Kohlen stoffatomes

Ladenburg (Ber 28 1995, (1895)) wies zum ersten Male darauf hin, daß die sogenannten $\alpha\ \gamma$ Diacipiperazine einen Fall darstellen, wo zwei asymmetrische Kohlen stoffatome nicht notwendigerweise optische Aktivitat veranlassen Nach van t Hoff kann dies nur eintreten bei racemischen Verbindungen und Verbindungen des Meso weinsauretypus wo die eine Halfte des Molekuls rechts drehend und die andere linksdrehend ist, die Aktivitat sich also aufhebt Der Fall der $\alpha\ \gamma$ Diacipiperazine laßt sich aber nicht so erklaren Sie haben die folgende allgemeine Formel



s Bischoff (Ber 2o, 29o0) und treten in den folgenden zwei stereoisomeren Formen auf

---

werden indem man auf Kartonpapier ein großes gleichschenkeliges Dreieck (20—20—15 cm) zeichnet und die Mittelpunkte der Seiten miteinander verbindet Das große Dreieck wird dann ausgeschnitten und an den Verbindungslinien des inneren Dreiecks zum Sphenoid zusammengefaltet Man macht zwei solche Modelle und unterscheidet die Ecken durch schwarze und rote Tinte so daß die Modelle Spiegelbilder von einander sind

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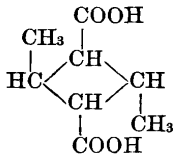
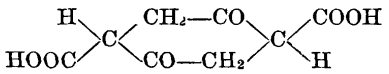
1) α-Thujaketosäure und ihrem Ammoniumsalz 54—56

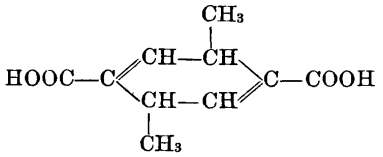
Andere ähnliche Fälle, von Hartwall (Diss Helsingfors 1904 S 10—13) und Aschan (Chemie der alicyklischen Verbindungen S 343—344) angeführt sind Trans dimethyl 1,3 cyklobutan trans dicarbonsäure 2,4



Trans succinylo bernsteinsäure (Ketoform)



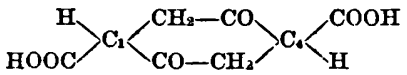
und Trans dimethyl 3,6 cyclohexadien 1,4 dicarbon säure 1 4



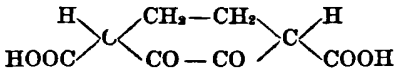
In jedem Falle ist das Molekül obwohl es wenigstens zwei asymmetrische Kohlenstoffatome und keine Symmetrieebene besitzt mit seinem Spiegelbilde identisch und somit inaktiv

Hartwall (l c) hat nun hervorgehoben, daß, obwohl die Molekule der angegebenen Art keine Symmetrieebene besitzen ihnen doch nicht alle Symmetrie fehlt In jedem Falle kann das Molekul durch eine Ebene in zwei gleiche Teile geteilt werden, von denen die eine Hälfte durch eine Drehung um 180° um die Achse dieser Ebene zum Spiegelbild der anderen Hälfte

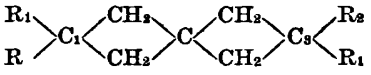
wird Eine solche Ebene nennt Groth (Ber 28 2510 (1895)) eine **Ebene der zusammengesetzten (indirekten) Symmetrie** Denkt man sich z B in der Trans succinylo bernsteinsaure



das Molekul auf der punktierten Linie halbiert und eine Halfte um 180° um die Achse $C_1 C_4$ gedreht so erhalt man dadurch die folgende Formel



in der die eine Halfte das Spiegelbild der anderen ist Wenn man nun aber die **aktive** Verbindung



betrachtet glaubt man zuerst daß sie auch eine Ebene der zusammengesetzten Symmetrie besitzt und zwar entlang der punktierten Linie Eine nahere Uberlegung oder Herstellung eines Tetraedermodells lehrt aber daß dies nicht der Fall ist Die Gruppen R_1 R_2 R_1 R_2 stehen wie schon hervorgehoben ist (S 8—9) gekreuzt zu einander Wenn man jetzt die eine Halfte des Molekuls um 180° um die Achse $C_1 C_3$ dreht wie es die Definition der zusammengesetzten Symmetrie fordert bleibt die gegenseitige Stellung der vier Gruppen unverandert

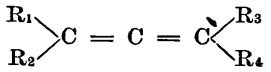
Hartwall (l c S 24) kommt nach einer sorgfaltigen Betrachtung der Frage zu dem Schluß

„Eine Verbindung ist optisch aktiv, wenn ihr Molekul — durch Tetraedermodelle dargestellt — nicht in eine Form gebracht werden kann welche eine oder mehrere Ebenen der einfachen oder der zusammengesetzten Symmetrie besitzt“

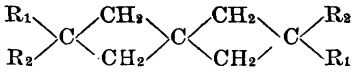
Dies kurzt Aschan (Chemie der alicyklischen Verbindungen S 346) folgendermaßen

„Ein Molekul ist asymmetrisch und zeigt optische Aktivitat, wenn es keine Ebene der einfachen oder zusammengesetzten Symmetrie besitzt“

Der Satz ist vortrefflich und hat den großen Vorteil uber den van t Hoffschen Satz, daß er ganz allgemein gultig ist Es muß aber nachdrucklichst hervorgehoben werden, daß in dem Vorhergehenden keine Widerlegung der van t Hoffschen Theorie zu erblicken ist, obwohl die Ansicht aufgegeben werden muß, daß optische Aktivitat nur in Verbindungen zu finden ist die ein oder mehrere Kohlenstoffatome des Typus $C(R_1R_2R_3R_4)$ besitzen van t Hoff selbst widerlegte diese Ansicht, als er optische Aktivitat in Verbindungen des Allylentypus voraussah denn in der Verbindung



ist kein Kohlenstoffatom, das mit vier verschiedenen Gruppen direkt gebunden ware Aus der optischen Aktivitat in diesem Typus ebenfalls optische Aktivitat in dem Typus



in einer Ebene, wie im Olefintypus, sondern in Ebenen liegen, die auf einander senkrecht stehen

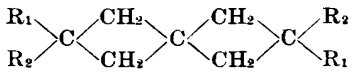
$$\begin{matrix} R_1 \\ R_3 + R_4 \\ R_2 \end{matrix}$$

Eine Verbindung von diesem Typus ist bisher meines Wissens noch nicht dargestellt worden

Die praktische Untersuchung hat in vollem Maße die Richtigkeit der Theorie bewiesen, denn, wie Landolt (Das optische Drehungsvermögen, II. Aufl. S. 46), sagt „Es zeigt sich, daß ausnahmslos die Aktivität mit dem Vorhandensein asymmetrischen Kohlenstoffes verbunden ist und daß Körper, welchen solcher fehlt, niemals Drehungsvermögen besitzen."

In den letzten Jahren hat sich aber herausgestellt, daß zwei wichtige Fälle von van't Hoff übersehen wurden. Ihrer Wichtigkeit wegen sollen sie hier erortert werden.

Aschan (Ber 35, 3396 (1902)) scheint zuerst darauf hingewiesen zu haben, daß für das Auftreten der optischen Aktivität bei Verbindungen des Allylentypus es nicht nötig ist, daß die vier Gruppen R_1, R_2, R_3, R_4 alle verschieden sein müssen, sondern daß die Bedingung der Asymmetrie durch den Typus



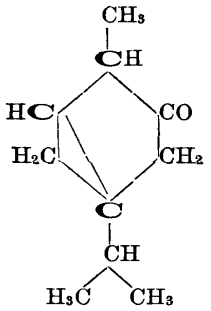
befriedigt wird, indem ein Tetraëdermodell einer solchen Verbindung mit seinem Spiegelbilde nicht zur Deckung gebracht werden kann [1]).

1) Die obige Asymmetrie kann folgendermaßen klar gemacht werden Die vier Gruppen R_1, R_2, R_1, R_2 stellen die Ecken eines tetraëdrischen Sphenoids dar Ein solches Sphenoid kann konstruiert

Aufgabe außerst einfach zu sein Mit Hulfe der modernen chemischen Methoden sind wir imstande, Verbindungen vom Typus $C(R_1R_2R_3R_4)$ darzustellen, deren Radikale wir fast nach Belieben wahlen konnen Man sollte meinen bestimmte Veranderungen der Konstitution einer solchen Verbindung wurden entsprechende regelmaßige Veranderungen des Drehvermogens veranlassen Es verhalt sich aber nicht so denn trotz der vielen Versuche auf diesem Gebiete muß das Gesetz uber die quantitativen Beziehungen zwischen chemischer Konstitution und Drehvermogen noch gefunden werden

Die nachfolgende Arbeit beschreibt, wie schon gesagt, Versuche in dieser Richtung mit verschiedenen Derivaten des Thujons Gleichzeitig wird eine kurze Zusammenfassung der Hauptversuche zur Losung der in dieser Arbeit beruhrten Probleme gegeben werden

Thujon ist ein Keton der Terpenreihe von der Formel



und besitzt drei asymmetrische Kohlenstoffatome Da samtliche asymmetrische Kohlenstoffatome verschieden sind, haben wir theoretisch 2^3 oder 8 optische Isomere zu erwarten, von welchen je 2 im Verhaltnis optischer

Antipoden zu einander stehen Bekannt sind nur zwei optisch isomere Formen von Thujon

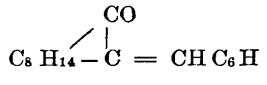
$$\alpha \text{ Thujon, } [\alpha]_D = -10\ 23$$
$$\text{und } \beta \text{ Thujon } [\alpha]_D = \text{ca } +70$$

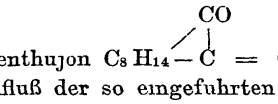
Vgl. Wallach. (Ann. 336 247 (1904)) und diese sind wie ihre Drehung zeigt, keine optischen Antipoden Diese Arbeit beschäftigt sich ausschließlich mit β Thujon, von Semmler Tanaceton genannt, da er es aus dem Tanacetol gewonnen hat.

Es ist natürlich von grundlegender Bedeutung bevor man versucht, das Verhältnis von chemischer Konstitution einer Verbindung und ihrer Drehung festzustellen daß die Konstitution der betreffenden Verbindung mit Sicherheit bekannt ist. Es kann hier nicht darauf eingegangen werden warum diese Formel des Thujons zugrunde gelegt wurde Sie ist aber die jetzt nach vielen Arbeiten von Wallach Semmler und anderen endgültig festgestellte Formel mit der sich alle unzähligen Umwandlungen des Thujons befriedigend erklären lassen Eine Zusammenfassung der Geschichte des Thujons findet man bei Wallach Terpene und Campher S 510 Semmler Die ätherischen Öle Bd. III, S 579 Aschan Chemie der alicyklischen Verbindungen S 187

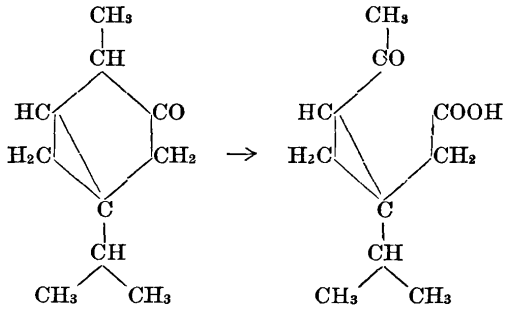
Thujon gibt bei der Behandlung mit Halogenalkylen nach der Grignardschen Reaktion eine Reihe tertiärer Alkohole

Durch Kondensation von Thujon mit Benzaldehyd nach Semmler (Ber 36 4367 (1903)) und Amylformiat nach Wallach (Ber 28 33 (1895)) und Steindorff (Diss Göttingen (1903)) wurden Benzylidenthujon



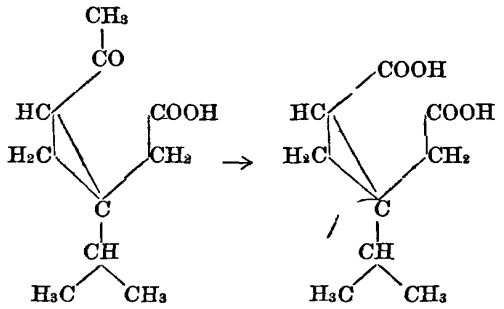
und Oxymethylenthujon  darge stellt Der Einfluß der so eingefuhrten Doppelbindung wurde unter Vergleich mit den Resultaten von Haller (Compt rend **136**, 1222 (1903), **142**, 316 (1906)) unter sucht

Wenn β Thujon bezw α Thujon mit verdunnter Kaliumpermanganatlosung oxydiert wird, erhalt man wie Wallach (Ann **273**, 113 **336**, 266—267) gezeigt hat, eine und dieselbe Ketosaure



Thujon α Thujaketosaure

Diese Ketosaure gibt ein charakteristisches Oxim und Semicarbazon Wenn man die Oxydation der Keto saure mit NaBrO fortsetzt, erhalt man nach Semmler (Ber **2**, 3348, (1892)) die entsprechende α Dicarbon saure



Die α Dicarbonsaure gibt mit Leichtigkeit ein Anhydrid

Es ergab sich daß der Dreiring in der α Dicar bonsaure im Gegensatz zu dem der α Thujaketosaure gegen verdunnte Salzsaure außerst bestandig ist Da her konnte die Dicarbonsaure durch Einleiten von trockenem Chlorwasserstoff in eine alkoholische Losung der Dicarbonsaure esterifiziert werden Eine Reihe von sechs Estern Dimethyl Diathyl Di n propyl Diisobutyl Diisoamyl und Monobenzylester wurde so dargestellt Diese Ester geben Natriumverbindungen deren Zerfallsprodukte auch untersucht wurden

Ein Versuch die α Thujaketosaure mittels Alkyl jodid und Silbersalz zu esterifizieren schlug fehl

Endlich wurde aus dem α Dicarbonsaureanhydrid das entsprechende Dicarbonsauremonamid dargestellt und ihre Drehungen bestimmt Zu Vergleichszwecken wurde die Drehung des Ammoniumsalzes der α Thuja ketosaure und des normalen und sauren Ammonium salzes der α Dicarbonsaure untersucht

Meine Arbeit hat demnach zum Gegenstand eine optische Untersuchung und — so weit die Verbindungen

noch unbekannt waren — eine chemische Bearbeitung betreffend

I Thujon, Thujylalkohol, Homothujylalkohol, Oxymethylen Thujon, Benzyliden Thujon

II α Thujaketosaure, Oxim und Semicarbazon der α Thujaketosaure

α Dicarbonsaure, Anhydrid der α Dicarbonsaure

III Dimethyl, Diathyl Di n propyl, Diiso butyl, Diisoamyl und Monobenzylester der α Dicar bonsaure

IV Monamid der α Dicarbonsaure, Ammoniumsalz derselben, saures Ammoniumsalz der α Dicarbonsaure, Normal Ammoniumsalz der α Dicarbonsaure, Ammo niumsalz der α Thujaketosaure

B 2) Arbeitsmethoden

Alle Drehungen wurden mittels eines Laurentschen Halbschattenpolarimeters (von Schmidt und Haensch Berlin) bestimmt Man konnte auf dem Instrument direkt halbe Grade ablesen und mittels eines Nonius auch Minuten Alle Ablesungen beziehen sich auf die Natriumflamme Da das Instrument keinen Thermostaten besaß, war es unmoglich, die Ablesungen bei einer konstanten Temperatur vorzunehmen Die Temperatur, bei welcher die Bestimmungen stattfanden, wurde aber immer notiert Die Mehrzahl der Ablesungen wurde zwischen 15° C und 18° C vorgenommen

Die Dichtebestimmungen wurden mit einer Mohr Westphalschen Wage ausgefuhrt und beziehen sich des halb auf Wasser von 15° C Falls wegen der Visko sitat einer Flussigkeit diese Methode nicht mehr zu verlassig war, wurde die Dichte mit Hulfe eines Pyknometers festgestellt Die verschiedenen Losungen

wurden in einem kleinen Erlenmeyerkolben unter genauem Abwagen hergestellt Nach dem Abwagen wurde die fest verkorkte Flasche mindestens 15 Minuten lang neben dem Polarimeter stehen gelassen Dies ist durchaus notig besonders bei Losungsmitteln mit großem Ausdehnungskoeffizienten da andernfalls in der Rohre Volumkontraktion oder Druck entstehen kann

Der angegebene Wert fur α_D ist in allen Fallen ein Mittelwert aus funf Ablesungen Die Ablesungen unter sich differierten selten um mehr als drei Minuten Der Nullpunkt des Instrumentes wurde am Anfang und am Ende jeder Beobachtungsreihe ermittelt und der Mittelwert genommen

Die Konzentration der verwendeten Losung mußte naturlich mit der Loslichkeit der betreffenden Substanz wechseln Gewohnlich wurden zwei Losungen hergestellt wenn moglich eine ca 5 %ige und eine ca 10 %ige (g pro 100 g Losung) In allen Fallen wo Vergleiche angestellt wurden sind die Drehungen bei annahernd gleicher Konzentration bestimmt

Samtliche Losungen wurden durch spatere Ablosungen auf das Eintreten von Mutarotation (Birotation) gepruft Das Zeitintervall zwischen Ablesung und Prufungsablesung wechselte zwischen mehreren Stunden und mehreren Monaten

B 3) Fehlerquellen

Die Mehrzahl der Ablesungen wurde wie schon oben gesagt mittels einer Mohr Westphalschen Wage ausgefuhrt daher kann die dritte Dezimalstelle nicht als genau angesehen werden Die Fehlergroße hangt von der Fluchtigkeit des Losungsmittels ab betragt aber meistens weniger als eine Einheit in der dritten

Dezimalstelle Da keine Flussigkeit eine geringere Dichte als 0,7 hatte, so ist der Fehler hochstens 1 in 700 Es muß hier wieder betont werden, daß die Dichten sich auf Wasser von 15° C beziehen

Die Fehler fur p sind die gewohnlichen Wagefehler Sie vergroßern sich mit der Fluchtigkeit des Losungsmittels und der Verdunnung der Losung Einen Fehler von 0 0002 g bei dem Abwagen berucksichtigend, findet man als Maximalfehler fur p in einer 5 %gen Losung nicht ganz 0, 001 oder weniger als 1 in 5000

Die wichtigste Fehlerquelle ist wohl in der Ablesung des Drehungswinkels zu erblicken Trotz der allergroßten Vorsicht bei der Ablesung und trotz der Annahme eines Mittelwertes aus funf Ablesungen ist ein Fehler von 1 Minute unvermeidlich Da dieses sich auch auf die Nullpunktbestimmungen des Apparates bezieht, muß der absolut unvermeidliche Fehler fur α_D gleich 2 Minuten oder 0, 033 Grad angegeben werden Fur spezifische Rotationen muß also immer in Betracht gezogen werden, daß der wahre Wert von α_D um 0 033 Grad großer oder kleiner als der gefundene sein kann Bei einem gefundenen Wert von $\alpha_D = 1, 00$ bedeutet dies einen unvermeidlichen Fehler von ungefahr 7 %

B 4) Abkurzungen

Es bedeutet im Folgenden

M das Molekulargewicht der aktiven Substanz
S Gewicht aktiver Substanz in Grammen
p Prozentgehalt aktiver Substanz in der Losung (g pro 100 g Losung)
c Prozentgehalt aktiver Substanz in der Losung (g pro 100 ccm Losungsmittel)

L Gewicht der Losung in Grammen
d das spezifische Gewicht der Losung bezogen auf Wasser von 15° C
t Temperatur des Beobachtungszimmers
l die Lange der Flu sigkeitssaule.
α_D den Mittelwert des abgelesenen Winkels
$[\alpha]_D = \frac{100\ \alpha_D}{l\ d\ p}$ die spezifische Drehung fur das Licht der Natriumflamme
$[M]_D = [\alpha]_D\ \frac{M}{100}$ die molekulare Drehung

Schlussfolgerungen aus den optischen Beobachtungen

A Einfluß des Uberganges CO → CHOH bzw CO → CROH Einfuhrung eines neuen asymmetrischen Kohlenstoffatomes

Es i t bekannt daß wenn man in einer inaktiven Verbindung ein Kohlenstoffatom zu einem asymmetrischen macht die resultierende Verbindung ein racemisches Gemisch von gleichen Mengen der rechts und links drehenden Formen ist Die Ursache hierfur liegt darin daß die Reaktionsgeschwindigkeit der Bildung der beiden Formen gleich ist Wenn aber das Ausgangsmaterial schon an und fur sich eine aktive Verbindung ist liegt ein anderer Fall vor Nehmen wir an daß das Ausgangsmaterial eine Drehung +A hat und wir ein neues asymmetrisches Kohlenstoffatom mit der Drehung ± B einfuhren so konnen wir zwei Formen erwarten eine mit der Drehung +A +B und eine mit der Drehung +A −B *Sie sind aber keine Spiegelbilder ondern*

chemisch und physikalisch verschieden Da die Bildungsgeschwindigkeit der beiden Formen höchst wahrscheinlich ganz verschieden ist, kann das Endprodukt ein Gemisch von den Formen +A+B und +A−B in beliebigem Verhältnis sein Wegen ihrer verschiedenen physikalischen und chemischen Eigenschaften wird man die optischen Komponenten häufig mechanisch trennen können

Im Thujon liegt der letztere Fall vor Mittels der Grignardschen Reaktion wurde Thujon in den entsprechenden tertiären Alkohol verwandelt Bei dieser Reaktion wird das Kohlenstoffatom der CO Gruppe asymmetrisch Bei der Umsetzung mit CH_3 Mg I konnte das Reaktionsgemisch durch Kühlung in eine feste links drehende (Smp 84) und eine flüssige rechtsdrehende Form getrennt werden Die feste Form entstand in viel geringerer Ausbeute als die flüssige Da die Trennung nur durch Abkühlen bewirkt werden konnte, war sie wohl nie vollständig, und die Flüssigkeit daher immer durch kleine Mengen der festen Form verunreinigt Es folgt daraus, daß die Drehungskonstanten der Flüssigkeit nur einen angenäherten Wert haben Da die eine Form des Homothujylalkohols fest war hoffte ich, daß dies auch bei den höheren Homologen der Fall sein würde, und es wurden daher die tertiären Alkohole mit der Äthyl , Propyl und Isopropylgruppe dargestellt Leider waren alle drei rechtsdrehenden Flüssigkeiten, die unscharf siedeten, und unter starkem Abkühlen keine feste Form ausschieden Da sie vermutlich Gemische von zwei optisch Isomeren sind, kann man ihren Drehungskonstanten keinen besonderen Wert beilegen Zu Vergleichszwecken wurde Thujylalkohol durch Reduktion von Thujon mittels Natrium in al

koholischer Losung dargestellt Das Resultat wai eine rechtsdrehende ziemlich konstant siedende Flussigkeit

	$[\alpha]_D$	$[\alpha]_l$ p = a 5 1 Ather	$[\alpha]_D$ p = ca 5 Methyl alkohol
β-Thujon	+ 67 4	+ 71 7	+ 68 0
Thujylalkohol		+ 56 6	+ 52 3
Homothujylalkohol (fest)		− 30 5	− 26 0
Homothujylalkohol (flussig)		ca + 35	ca + 33

Der einzige sichere Schluß den wir aus den obigen Zahlen ziehen konnen ist daß die Umwandlung von CO in CHOH das optische Drehvermogen vermindert Eine Verminderung des Drehvermogens bei diesem Uber gang findet wie die folgenden Zahlen zeigen ziemlich allgemein statt Sie ist wohl auf die Aufhebung der Carbonyl Doppelbindung zuiuckzufuhren

		$[\alpha]_D$
β Thujon	p = ca 5 in Ather	+ 71 7
Thujylalkohol		+ 56 6
Methyl 1 cyklopentanon 3 [1])		+ 13ɔ 9
Methyl 1 cyklopentanol 3 [1])		− 4 89
D Fenchon)	p = 1? 93 in Athylalkohol	+ 72
D l Fenchylalkohol)	p = 1ɔ 66	− 10 3ɔ
L Fenchon [3])	p = ?	− 72
L d Fenchylalkohol [3])	p = 12 88	+ 10 35
Nopinon)	p = ca 7 in Ather	+ 11 02
α Nopinol [4])	p = 12 ɔ3	− ɔ 32
β Nopinol [4])	p = 13 1ɔ	− 1ɔ 03

1) Zeit ky Ber 3 2494 682 (190)
) Wallach A 63 132 145 (1891)
3) 7? 104 (189)
4) 356 3 238 (1907)

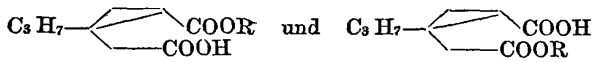
D Campher[1])	p = ca 20	in Athylalkohol	+ 42
D Borneol[2])	p = ca 20 „	„	+ 37,44
L Campher[1])	p = ca 20 „	„	− 42
L Borneol[2])	p = ca 20 „	„	− 37 44

Man darf aber nicht vergessen, daß in den Fallen, wo bei der Reduktion nur ein sekundarer Alkohol ent steht, das erhaltene Produkt ein Gemisch von zwei optischen Isomeren sein kann Diese Moglichkeit bietet auch eine Erklarung fur die Erniedrigung der Drehung

B Einfluß homologer Kohlenwasserstoff radikale

Da der Dreiring in der α Dicarbonsaure im Gegen satz zu dem der α Thujaketonsaure sich als sehr be standig gegen verdunnte Salzsaure erwiesen hatte, war es moglich geworden die Dicarbonsaure in der gewohn lichen Weise zu esterifizieren namlich durch Einleiten von HCl Gas in eine Losung von Dicarbonsaure in dem betreffenden Alkohol Mit dem Methyl , Athyl und n Propylalkohol ging die Esterifikation glatt von statten und reine, normale Ester wurden gewonnen Mit dem Isobutyl und Isoamylalkohol dagegen ging sie nicht so leicht vor sich In diesen beiden Fallen wies das Resultat der Analyse trotz tagelanger Esterifikation und wiederholtem Fraktionieren des erhaltenen Pro duktes darauf hin daß Spuren von irgend welcher Verunreinigung, wahrscheinlich von saurem Ester, vor handen waren Der Versuch einen Dibenzylester dar zustellen, ergab einen Monobenzylester der ein Gemisch von zwei isomeren Formen sein kann

1) Landolt l c S 564
2) l c S 558 559



Die Zahlen fur die drei letzten Verbindungen namentlich fur den Diisoamylester sind also nur als angenahert zu betrachten Da der verwendete Amylalkohol eine Linksdrehung von $\alpha_D = -1\,1$ ($l = 1$ dm) aufwies muß der Ester entsprechend niedrig drehen Der wahre Wert von $[\alpha]_D$ fur diesen Ester ist also hoher als der gefundene Der Benzylester bietet sehr wahrscheinlich einen interessanten Fall von sterischer Hinderung

Im folgenden die Zahlenangaben

	$[\alpha]_D$	$[M]_D$	Diff	$[\alpha]_D$ p = c 5 i Ather	$[M]_D$ Ather	Diff
α Dicarbonsaure				+105	+195 4	+108 6
Dimethylester	+142	+304 0	−28	+142	+304 0	− 25 5
Diathylester	+114	+276 1	−47	+115	+278 5	− 48 8
Di n propylester	+ 84 7	+228 9	+ 2	+ 85	+229 7	− 16 2
Diisobutylester	+ 77 6	+231	+ 9	+ 71 6	+213 5	+ 25
Diisoamylester	+ 73 5	+240		+ 73 1	+238 5	
Monobenzylester				+ 35 0	+ 96	

Die Ergebnisse zeigen daß der Ubergang von Saure in Methylester ein Steigen der molekularen Drehung um 108 Einheiten herbeifuhrt Die Wirkung der Substitution wird dann schnell schwacher mit steigendem Molekulargewicht des Alkylradikals Bei dem Di n propylester wird ein Minimum der molekularen Drehung deutlich erreicht dann fangt sie wieder an zu steigen Viele Falle sind schon bekannt von einem Maximum der molekularen Drehung in homologen Reihen Ein anderes Beispiel von einem Minimum ist meines Wissens noch nicht beobachtet worden

Die spezifische Drehung nimmt ab vom ersten Glied an

Im folgenden die Zahlen fur die Ester der Camphersaure

		$[\alpha]_D$	$[M]_D$
D Camphersaure (p = 15 in abs Alkohol)[1]		+47,35	+ 94,6
Dimethylester	(reine Substanz)[2]	+48,16	+109,9
Diathylester	(„ „)[2]	+36,30	+ 84 3

Hier sieht man dasselbe Phanomen — ein Steigen der spezifischen und molekularen Drehung beim Ubergang von Saure in Methylester und ein Sinken beim Uber gang von Methylester in Athylester Die Wirkung des Uberganges von Saure in Methylester ist hier allerdings verschwindend klein

Der Unterschied der spezifischen Drehung zwischen dem normalen und dem sauren Methylester der Campher saure ist, wie aus den folgenden Zahlen erhellt, klein

		$[\alpha]_D$
al Methylester[3]	C_8H_{14} COOH $COOCH_3$	+ 43,5
o Methylester[3]	C_8H_{14} $COOCH_3$ COOH	+ 51 5
Dimethylester[3]	C_8H_{14} $COOCH_3$ $COOCH_3$	+ 44,4

Uber den Einfluß eintretender Alkylgruppen in das Bornylamin liegt eine ausfuhrliche Untersuchung von Forster vor (Journ Chem Soc 75, 934 (1899))

	$[\alpha]_D$	$[M]_D$	$[M]_D$ in Benzol	Diff
Bornylamin	—	—	+ 87,3	
Methylbornylamin	+ 96,8	+ 161,6	160 1	+72,8
Athylbornylamin	93 0	168 3	163,4	+ 3,3
n Propylbornylamin	89,0	173,5	169,8	+ 6,4
Butylbornylamin	81,7	170,7	167,8	− 2,0

1) Landolt l c S 572
2) Bruhl und Braunschweig Ber 25 1801 (1892)
3) Haller Compt rend 114 1516

Das Maximum der spezifischen Drehung findet hier auch wie unter den Estern der α Dicarbonsaure beim ersten Glied der Reihe statt Dagegen zeigt die Propylverbindung das Maximum der molekularen Drehung

Die folgenden Zahlen von Binz (l c S 38 und Zeit Phys Chem 12 727 (1893)) verdeutlichen den Einfluß eintretender Acylgruppen in das Menthylamin und Fenchylamin

	$[\alpha]_D$	$[M]_D$	Diff
Menthylamin (aus Links Menthon) reine Subst	− 38 07	− 58 90	
Formylmenthylamin in Chloroform	− 83 37	− 152 27	+ 93 37
Acetylmenthylamin	− 81 81	− 160 84	+ 8 57
Propionylmenthylamin	− 76 53	− 161 15	+ 0 31
Butyrylmenthylamin	− 72 10	− 161 90	+ 0 75
Fenchylamin (aus Rechts Fenchon) reine Subst	− 24 89	− 38 00	
Formylfenchylamin in Chloroform	− 36 56	− 66 04	+ 28 04
Athylfenchylamin	− 46 62	− 90 73	+ 24 69
Propionylfenchylamin	− 53 16	− 110 88	+ 20 15
Butyrylfenchylamin	− 53 11	− 118 19	+ 7 31

Die Ergebnisse fur die Acylmenthylamine sind im großen ganzen analog denen fur die Alkylbornylamine Man hat hier wieder ein Maximum der spezifischen Drehung beim ersten Glied der Reihe die molekulare Drehung hat aber statt ein Maximum bei der Propylverbindung zu zeigen vielleicht ihr Maximum bei der Butyrylverbindung noch nicht erreicht

Die Resultate fur die Acylfenchylamine sind von beiden vorhergehenden abweichend Hier steigt sowohl die spezifische als auch die molekulare Drehung vom ersten Glied an Die spezifische Drehung erreicht ein

Maximum bei der Propylverbindung, das Maximum de molekularen Drehung dagegen ist bei der Butyrylver bindung offenbar noch nicht erreicht worden

Von einem konstanten Zuwachs der Mole kularrotation kann niemals die Rede sein

Walden (Ber 38, 355 (1905)) gibt eine Zusammen fassung der Resultate fur molekulare Drehung in homo logen Reihen Nach ihm kann man haben

I Einen Aufstieg des molekularen Drehungsvermogens zum Maximum und alsdann Konstanz

II Einen Aufstieg zum Maximum mit nachheriger Ab nahme der Molekularrotation

III Eine Konstanz der Molekularrotation bezw das erste Glied zeigt ein geringes Maximum, und fur die weiteren Reihenglieder ist die Molekularrotation praktisch konstant

IV Einen Abfall der Molekularrotation vom ersten Glied an

Wir durfen wohl hinzufugen

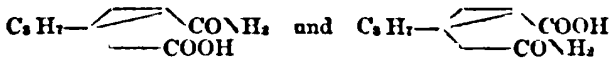
V Einen Abfall zum Minimum mit nachheriger Zu nahme der Molekularrotation

Mit einem Worte, die Veranderung der mole kularen Drehung in homologen Reihen wech selt sowohl qualitativ als quantitativ von Reihe zu Reihe In ein und derselben Reihe besteht aber immer ein ausgepragter quali tativer Zusammenhang zwischen den Resul taten

C Einfluß der Amido und Hydroxylgruppe

van t Hoff (l c S 122) weist darauf hin, daß bei vierzehn Amidosauren hauptsachlich der aliphatischen Reihe durchweg eine ziemlich geringe Drehung beobachtet

wurde Es fragt sich ob der Übergang von COOH $\rightarrow$ CONH$_2$ immer eine Erniedrigung der Drehung bewirkt Um diese Frage weiter zu studieren wurde das Monamid der α Dicarbonsäure durch Addition von NH$_3$ an α Dicarbonsäure-Anhydrid dargestellt Es war anzunehmen daß durch eine solche Reaktion zwei Verbindungen entstehen würden die sich durch die Stellung der Amidogruppe unterschieden



Nur ein Monamid konnte gewonnen werden Es ist nach seinem scharfen Schmelzpunkt und ausgeprägt kristallinischen Charakter zu urteilen eine einheitliche Substanz und kein Gemisch Da die Ausbeute stets klein war ist das Vorhandensein einer zweiten Verbindung in der Mutterlauge sehr wohl möglich Welche der beiden möglichen Formen in der erhaltenen Substanz vorliegt, läßt sich noch nicht entscheiden.

Die spezifische Drehung des Monamids und seines Ammoniumsalzes sei mit der der Ammoniumsalze der α Thujaketosäure und α Dicarbonsäure verglichen

Ein Versuch durch Addition von Anilin und Piperidin aus dem Anhydrid die entsprechenden Anil und Piperidilsäuren darzustellen schlug fehl

		$[\alpha]_D$ (in Wasser)	$[\alpha]_D$ (in Methylalkohol	
α Thujaketosäure	p = 0 6754	+244	+215	(p = 5)
α Thujaketosaures Ammonium	p = 0 881	+171		
α Dicarbonsäure	p = 0 7323	+135	+104	(p = 5)
Sauer α Dicarbonsaures Ammonium	p = 0 793	+ 15 2		

		$[\alpha]_D$ (in Wasser)	$[\alpha]_D$ (in Methyl alkohol)
Normal α Dicarbonsaures Ammonium	p = 1,9	−7,1	
Normal α Dicarbonsaures Ammonium	p = 3,8	−5,35	
Monamid der α Dicarbon säure			+54 5 (p = 3,77)
Ammoniumsalz des Monamids	p = 1,713	−17,6	+ 9,2 (p = 4,694)

Man sieht, daß in der Tat der Übergang von Dicarbon saure zur Amidosaure eine Erniedrigung der spezi fischen Drehung fast auf die Halfte zur Folge hat In jedem Falle auch ist die Drehung der Ammonium salze viel niedriger als die der freien Saure

Andere Beispiele derselben Art sind nicht schwer zu finden

l Mandelsaure [1]) c = 2,50 in Aceton $[\alpha]_D^{22} = -148$
Mandelsaureamid [1]) c = 2,50 in Aceton $[\alpha]_D^{22} = -66,6$
Citronellasaureamid [2])
p = 8,742 in Ather (l = 1 dm) $\alpha_D = +0^0,25',6$
Menthonensaureamid [2])
p = 8,784 in Ather (l = 1 dm) $\alpha_D = +0^0,24',8$

Vgl auch van t Hoff l c

Wenn aber die Saure selbst ein geringes Dreh vermogen besitzt, kann die Uberfuhrung in Amid er hohend auf die Drehung wirken

z B			$[\alpha]_D$
Apfelsaure	Wasser	c = ca 5	− 2,6
Apfelsaurediamid [3])	„	c = 4,32	−37,6

1) Walden Zeitschr f phys Chem 17 706
2) Wallach Ann 296 125 (1897)
3) Landolt l c S 477 und 481

D Camphersaure[1]) $C_8H_{14}(COOH)_2$ abs Alkohol
p = 15 + 47 3o

β Monamid $C_8H_4(COOH)CO\diagdown NH_2$ abs Alkohol + 60

Also erfolgt die Wirkung des Uberganges $COOH \rightarrow CO\diagdown NH_2$ nach keiner allgemeinen Regel

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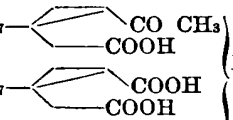
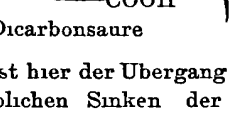
Bei Alkoholen vom Typus $CH_2OH(CHOH)CH_2OH$ und Oxysauren speziell bei den Sauren vom Typus $CH_2OH(CHOH)_4COOH$ anfangend bei der Glycerin saure ist wie van t Hoff (l c) gezeigt hat das Dreh vermogen auffallend klein Im Laufe dieser Arbeit stieß ich auf mehrere Beispiele wo die Einfuhrung einer Hydroxylgruppe eine ausgesprochene Erniedrigung des Drehvermogens zur Folge hatte

Z B		$[\alpha]_D$	$[M]_D$
α Thujaketosaure C_3H_7— 	p = ca 5 % in Ather	+194	+357
α Dicarbonsaure C_3H_7— 		+10o	+19o
Dimethylester der α Dicarbonsaure		+142	+304

Wie ersichtlich ist hier der Ubergang $CO\ CH_3 \rightarrow COOH$ mit einem erheblichen Sinken der Ubergang $COOH \rightarrow COOCH_3$ mit einem bedeutenden Steigen der spezi fischen und molekularen Drehung verbunden

Dasselbe findet man in den folgenden Zahlen die den Ubergang $CO \rightarrow C = NOH \rightarrow C = N—NH_2$ $CO\diagdown NH_2$ verdeutlichen

---

1) La dolt l c S 5 u d 5 4

			$[\alpha]_D$	$[M]_D$
α Thujaketosaure	p = 4,61	in Eisessig	+ 224	+ 412
Oxim (Smp 174 175)	p = 1,7008	„ „	+ 5,56	+ 11,07
Semicarbazon	p = 2,29	„ „	+ 227	+ 547

Wie schon hervorgehoben ist findet man auch schließlich ziemlich allgemein eine Erniedrigung der Drehung beim Ubergang CO → CHOH

Samtliche Tatsachen wurden eine einfache Erklarung finden konnte man annehmen, daß eine Hydroxylgruppe immer einen erniedrigenden Einfluß auf die Drehung ausubt

Dies ist aber nicht der Fall Der Ubergang CO → C = NOH kann eine Erhohung einer Rechts bezw Linksdrehung bewirken

Z B			$[\alpha]_D$
β Thujon	Methylalkohol	p = ca 5	+ 68
Oxim [1])	„	(p = ?)	+ 105
α Thujon [2])	(reine Substanz)		− 10,23
Oxim [3])	Ather	(p = 33 76)	− 29,25

Manche viele Hydroxylgruppen enthaltende Korper wie die Aldehydzucker Inosit u s w weisen eine ziemlich starke Drehung auf

Die Wirkung der Hydroxylgruppe erfolgt also wie die der Amidogruppe, nach keiner allgemeinen Regel

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1) Wallach Ann 336 247
2) 336 263
3) 336 266

D Einfluß der Ringbindung

Uber den Einfluß der Ringbindung auf die Drehung liegt eine Fulle von Material vor In der aliphatischen Reihe wurde der Ubergang von einfacher zu doppelter Bindung von Walden (Zeitschr f phys Chem 20 o69 (1896)) an einer Reihe von flussigen Estern des Links Amyalkohols studiert. Er findet daß in jedem Falle der Ubergang zur Doppelbindung eine Erhohung des Drehvermogens zur Folge hat Beim Ubergang von doppelter zu dreifacher Bindung tritt in dem einzigen untersuchten Falle wieder eine Abnahme der Aktivi tat ein

Wir entnehmen folgendes

	$[\alpha]_D$	$[M]_D$	Diff
$(CH_3)_2CH—COOC_5H_{11}$	+3 10	+ 4 90	+ 0 o7
$CH_2 = C(CH_3)—COOC_5H_{11}$	+3 51	+ o 47	
$C_6H_5\ CH_2\ CH_2\ COOC_5H_{11}$	+2 26	+ 4 98	+11 4
$C_6H_5\ CH = CH—COOC_5H_{11}$	+7 51	+16 38	− 4 33
$C_6H_5\ C \equiv C—COOC_5H_{11}$	+o 58	+12 05	

Wie ersichtlich variiert der Mehrbetrag ganz be deutend In der alicyklischen Reihe wurde dieselbe Frage durch Haller und seine Schuler[1]) Zelinsky[2]) Rupe[3]) Klages und Sautter[4]) und Hilditch[5]) bear beitet

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1) Compt re d **128** 1370 (1899) **129** 1006 (1900) **136** 1 22 1613 (1903) **142** 316 (1906)

2) Ber **34** 3 55 (1901) **35** 2488 (190)

3) A n **327** 157 (1903)

4) Ber **37** 649 (1904) **38** 231 (190) **39** 1938 (1906) Jo n Chem S c **93** 1 00 (1908)

Die folgenden Zahlen von Hilditch (Journ Chem Soc 93, 700 (1908)) verdeutlichen den Einfluß des Uber ganges von einfacher zu doppelter und von doppelter zu dreifacher Bindung Das Losungsmittel war in jedem Falle Chloroform, p ca. 4 % X stellt die be treffende Base dar

	$[\alpha]_D$ Conin	$[\alpha]_D$ Brucin	$[\alpha]_D$ Kodin	$[\alpha]_D$ Cinchonin
$C_6H_5—CH_2—CH_2$ COO X	−1,87	−38,19	−64,37	+116,25
$C_6H_5—CH = CH$ COO X	−7,50	−11 68	−51,63	+107,50
C_6H_5 $C \equiv C$ COO X	−7 12	+ 3,33	−51	+ 86

Man sieht daß hier abgesehen von den Conin Salzen, der Ubergang von einfacher zu doppelter Bindung eine Verminderung des Drehvermogens bewirkt Eine Erklarung fur diesen Widerspruch mit der Waldenschen Angabe findet man bei der Betrachtung der Zahlen fur die Drehung der betreffenden Basen Um den Vergleich zu erleichtern sind die Zahlen fur das Phenylpropion saure Salz wiedergegeben

		$[\alpha]_D$	$[\alpha]_D$ (Phenylpropion saures Salz)
Conin	(freie Base)	+ 8	− 1,87
Brucin	(„ „)	−122	− 38,19
Kodin	(„ „)	−115 63	− 64,37
Cinchonin	(p = 0,5 in Alkohol)	+222	+116,25

Bei der Salzbildung wird also in jedem Falle die spe zifische Drehung vermindert, und der Ubergang von einfacher zu doppelter Bindung verstarkt nur den Ein fluß der Salzbildung Genau dasselbe findet man bei den Waldenschen Resultaten Der schwach linksdre hende Amylalkohol gibt mit den verwendeten gesattig

ten Sauren rechtsdrehende Ester Das Esterifizieren hat also einen Ubergang von links nach rechts bewirkt Dieser Einfluß wird beim Ubergang von gesattigtem Ester zu ungesattigtem Ester verstarkt

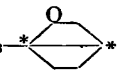
Abgesehen von dem Falle des phenylpropiolsauren Cinchonins hat der Ubergang von einfacher zu doppel ter Bindung in Ubereinstimmung mit dem Waldenschen Re ultate einen großeren Einfluß ausgeubt als der Uber gang von doppelter zu dreifacher Bindung

Die folgenden interessanten Zahlen von Rupe (Ann 327 166 (1903)) zeigen wie der Einfluß der Doppel bindung auf die Drehung mit ihrer Entfernung vom asymmetrischen Kohlenstoffatom abnimmt

Menthyle ter der	$[\alpha]_I$	$[M]_D$
Crotonsaure	— 90 67	— 203 1
$\alpha\beta$ Pentensaure	74 41	177 1
$\beta\gamma$	72 51	172 5
$\gamma\delta$	67 32	160 2
$\alpha\beta$ Hexensaure	68 38	172 4
$\beta\gamma$	65 11	164 1
$\gamma\delta$	60 93	153 5
$\delta\varepsilon$	61 25	154 4
$\alpha\beta$ Heptensaure	66 03	177 5

Haller und Muller (Compt rend 128 1372 (1899)) geben die folgenden interessanten Zahlen fur Derivate des Camphers

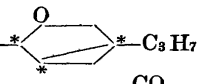
$[\alpha]_D$

Campher CH_3—  * (absolut Alkohol) ca $\sim$+42

Asymmetr sche Kohle stoffatome

			$[\alpha]_D$
Benzylidencampher			
$C_8H_{14}-\overset{\overset{\displaystyle CO}{\|}}{C}=CH\ C_6H_5$	p = 6 78	Toluoll	+429
p Methoxybenzylidencampher	p = 7,60	„	+467
m Methoxybenzylidencampher	p = 7,65	„	+379
Piperonylidencampher			
$C_8H_{14}-\overset{\overset{\displaystyle CO}{\|}}{C}=CHC_6H_3<\begin{smallmatrix}O\\O\end{smallmatrix}>CH_2$	p = 4,04	Toluoll	+435
Cuminylidencampher			
$C_8H_{14}-\overset{\overset{\displaystyle CO}{\|}}{C}=CH\ C_6H_4\ C_3H_7$	p = 4 02	„	+496

Diese enorme Veranderung der Drehung bis zur zehn fachen Drehung der ursprunglichen Substanz wieder holt sich bei den Resultaten, die Haller (Compt rend **140**, 1626 (1905)) mit den entsprechenden Derivaten des Thujons erhielt Hier geht aber die Veranderung genau in entgegengesetzter Richtung vor sich Eine ziemlich hohe Rechtsdrehung wird in eine enorm hohe Links drehung umgewandelt

			$[\alpha]_D$
β Thujon 	p = 5,17	in Methyl alkohol	+68
Benzylidenthujon $C_8H_{14}-\overset{\overset{\displaystyle CO}{\|}}{C}=CH\ C_6H_5$	p = ca 3¹/	in Athyl alkohol	−590
p Methoxybenzylidenthujon			−829
Piperonylidenthujon			−765

Der gewaltige Einfluß der Gruppe = CHR hangt viel

* Asymmetrische Kohlenstoffatome

leicht mit ihrer Lage in Bezug auf die asymmetrischen Kohlenstoffatome zusammen In beiden Reihen haben wir die Gruppierung C—CO—C = (CHR)—$\overset{*}{C}$ wo die Endkohlenstoffatome asymmetri ch sind

Sehr beachtenswert in dieser Beziehung sind die folgenden Zahlen von Binz (Diss Gottingen (1893) S 37 und Zeitschr f phys Chem **12** 727 (1893))

	$[\alpha]_D$
Fenchylamin (reine Substanz)	− 24 89
Benzylidenfenchylamin p = 5 71 in Chloroform	+ 73 14
p Methoxybenzylidenfenchylamin p = 4 97 in Chloroform	+ 78 10

Von dem enormen Einfluß der = CHR Gruppe ist hier nichts zu sehen Uber den Bau des Fenchylamins bestehen noch verschiedene Ansichten Sicher ist aber daß man es hier mit der Gruppierung $\overset{*}{C}$—CH (N = CHR) zu tun hat Ob der schwachere Einfluß der = CHR Gruppe auf die großere Entfernung vom asymmetri schen Kohlenstoff oder auf die Verknupfung durch Stickstoff oder auf beides zuruckzufuhren ist laßt sich noch nicht entscheiden

Der Einfluß der Doppelbindung im Gegensatz zu dem der Phenylgruppe ist durch die folgenden Zahlen verdeutlicht (Haller Compt rend **142** 319 (1906))

			$[\alpha]_D$
Campher	(absolut Alkohol)	ca	+ 42
Hexahydrobenzylcampher	( )		+ 55
Benzylcampher	( )		+ 144
Benzylidencampher	( )		+ 425

Man sieht daß der steigernde Einfluß der

Asymmet che Kohle t ffat e

Doppelbindung viel großer als der der Phenylgruppe ist Bei der Betrachtung der obigen Zahlen darf aber nicht vergessen werden, daß bei der Reduktion von Benzyliden zu Benzylcampher ein neues asymmetrisches Kohlenstoffatom eingefuhrt wird Die Reduktionsprodukte konnen also Gemische von zwei Isomeren sein

Um mit den Resultaten von Haller in der Thujon reihe Vergleiche anstellen zu konnen, wurde Oxymethylenthujon nach der Vorschrift von Wallach (s Steindorff, Diss Gottingen (1903)) und Benzylidenthujon nach Semmler (Ber **36**, 4367 (1903)) dargestellt

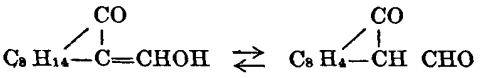
Es ergaben sich die folgenden Resultate

			$[\alpha]_D$
Oxymethylenthujon	C_8H_{14}—C(CO)=CHOH	p = ca 5 in Methyl	−10 1
Benzylidenthujon		Alkohol	−591

Wie ersichtlich, stimmt das Resultat fur Benzylidenthujon mit der Angabe von Haller vortrefflich uberein, obwohl die Darstellungsmethoden verschieden waren Das Oxymethylenthujon zeigte Mutarotation

Frisch dargestellt	(reine Substanz)	(l = 1 dm)	$\alpha_D = -12{,}16$
Nach 48 Stunden	(konstant)	(l = 1 dm)	$\alpha_D = -10\,566$
			$[\alpha]_D = -10{,}34$

Der kleine Einfluß der Doppelbindung in Oxymethylenthujon im Vergleich zum abnorm hohen Einfluß bei der Benzylidenverbindung ist sehr auffallend Die Existenz der Mutarotation und das niedrige Drehvermogen wurden eine befriedigende Erklarung finden, wenn man annehmen konnte daß teilweise eine Umwandlung zum Aldehyd unter Aufhebung der Doppelbindung nach der Erlenmeyerschen Regel stattgefunden hatte



Hier sind die folgenden Zahlen am Platze

			$[\alpha]_D$
α Thujaketosaure	p = 4 61	in Eisessig	+ 224
Oxim Smp 174—175	p = 1 70		+ 5 56
Semicarbazon	p = 2 29		+ 227

Man sieht daß die Umwandlung von C = O in C = NOH eine Verminderung der spezifischen Drehung um fast 220 Grad hervorruft wahrend die Umwandlung von CO in C = N NH CO NH_2 fast gar keinen Einfluß ausubt

Ringschluß

Der Einfluß des Ringschlusses wurde allein im folgenden Beispiel untersucht

			$[\alpha]_D$
α Dicarbonsaure	p = 2 87	in Chloroform	+ 171
Anhydrid	p = 4 06		+ 10 1

Aschan (Ber 27 2011 (1894)) fand ahnliche Resultate fur Camphersaure und ihr Anhydrid

		$[\alpha]_D$
Camphersaure	(Alkohol)	ca + 50
Anhydrid	(Chloroform)	0
	(Benzol)	schwach

In diesen beiden Fallen erfolgt mit der Bildung eines Anhydrids aus einer Dicárbonsaure eine starke Erniedrigung der Drehung d h ein Ubergang nach links Haufig hat der Ringschluß die entgegengesetzte Wirkung namlich einen Ubergang nach recht zur Folge z B

			$[\alpha]_D$
Diacetylweinsaure [1])	c = 3 27	in Athylalkohol	− 21,[illegible]
Anhydrid [1])	c = 4,40	in Aceton	+ 62 [illegible]
Dibenzoylweinsaure [1])	c = 4,76	in Athylalkohol	− 117 [illegible]
Anhydrid [1])	c = 4 04	in Aceton	+ 142 9

Der Ringschluß kann aber auch eine Erhohung einer Rechts bezw einer Linksdrehung bewirken

β Methyladipinsaure athylester [2])

$$\begin{array}{l} CH_2 \quad CH_2 \quad COOR \\ \quad | \\ CH_3\,CH \quad CH_2 \quad COOR \end{array}$$

$\alpha_D = +2^0\,30$ (l = 1 dm)

→

Methyl 1 cyklopentanon 3 carbonsaure 4 athylester [2])

$$\begin{array}{l} CH_2 \text{———} CH \quad COOR \\ \quad | \qquad\qquad\quad | \\ CH_3\,CH\text{—}CH_2 \quad CO \end{array}$$

$\alpha_D = +82^0\,20$ (l = 1 dm)

Arabonsaure → Arabonsaure Lakton

$CH_2\,OH\,(CHOH)_3\ COOH$

$[\alpha]_D$ = ca − 8 [3])

$[\alpha]_D = -74$ [4])

Tabellen, die den Einfluß der Laktonbildung bei den Sauren der Zuckerreihe zeigen, werden von Landolt (l c S 264) und van t Hoff (l c S 110) angefuhrt Landolt sagt „Das Drehungsvermogen ring formig konstituierter Laktone erweist sich somit als sehr viel starker als dasjenige der Saure Jonen und oft in der Richtung entgegengesetzt Die Drehungsanderung betragt meist 100 bis 150 Bestimmte Zahlen regelmaßigkeiten lassen sich nicht erkennen“

Man kann die Ergebnisse fur den Einfluß der Ring bindung auf die Drehung folgendermaßen zusammen fassen

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1) Pictet Jahresb 1882 S 856
2) Haller und Desfontaines Compt rend **136** 1013 (1903)
3) Ann **260** 313
4) Ber **24** 4217

1 Der Ubergang von einfacher zu doppelter Bindung hat gewohnlich eine starke Anderung der Drehung zur Folge Die Richtung dieser Anderung variiert mit der aktiven Substanz

Der Betrag der Anderung nimmt mit der Entfernung der Doppelbindung vom asymmetrischen Kohlenstoff ab

2 Die Gruppierung $\overset{*}{C}$—CO—C=(CHR)—C bei der die Endkohlenstoffatome asymmetrisch sind und R einen Benzolring enthalt scheint die vermehrende Wirkung der Doppelbindung auf die Drehung außerordentlich zu verstarken

3 Der Ubergang von doppelter zu dreifacher Bindung ubt gewohnlich einen verhaltnismaßig geringen Einfluß aus

4 Ringschluß bei Anhydriden wie bei Laktonen veranlaßt immer eine ausgesprochene Anderung der Drehung Die Richtung dieser Anderung folgt aber keiner allgemeinen Regel

E Schlußfolgerung

Die Resultate sind nicht vom Standpunkt der Guye Crum Brownschen Hypothese betrachtet worden und zwar aus zwei Grunden

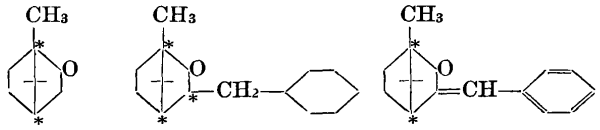
Erstens Wir haben es nur mit Ringverbindungen zu tun gehabt auf welche die Guye sche Formel fur die Berechnung des Asymmetrieproduktes nicht anwendbar ist

Zweitens Die Resultate der neueren Untersuchungen sind im ganzen fur die Hypothese ungunstig

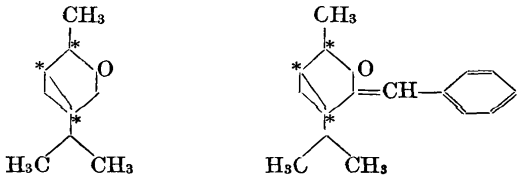
und haben zur Erkennung der Tatsache geführt, daß der Einfluß einer Gruppe auf die Drehung nicht nur von ihrer Masse, wie Guye annahm sondern ebensoviel wenn nicht mehr von ihrer eigenen Natur der anderen Gruppen im Molekul abhangt

Am Ende jedes Kapitels ist eine Zusammenfassung der betreffenden Resultate gegeben worden und es ist also unnotig, diese hier zu wiederholen Doch mochte ich wiederum betonen

Erstens Den enormen Einfluß der Ringbindung speziell der Doppelbindung auf die Drehung Die Resultate von Haller machen dies am besten klar



Campher Hexahydrobenzylcampher Benzylidencampher
$[\alpha]_D = +42$ $[\alpha]_D = +55$ $[\alpha]_D = +429$



β Thujon Benzylidenthujon
$[\alpha]_D = +68$ $[\alpha]_D = -590$

Es drangt sich sofort die Frage auf was ist eine chemische Bindung? Fur diese Frage gibt es bis jetzt keine befriedigende Antwort Der außerordentliche

** Lage der asymmetrischen Kohlenstoffatome

Einfluß der Doppelbindung auf die Drehung kann vielleicht der Schlussel zur Losung dieses Problems werden

Zweitens In jeder gegebenen Reihe von Verbindungen besteht ein deutlich ausgesprochener qualitativer Zusammenhang zwischen den Resultaten aber niemals ein quantitativer Dieses Resultat ist um so auffallender wenn man bedenkt daß die anderen optischen Eigenschaften wie das Brechungsvermogen und die magnetische Rotation additiven oder konstitutiven Charakters sind Man fuhlt sich zu der Frage gedrangt ob der Fehler nicht an unserer Vergleichungsweise liegt Sicher ist daß die Vergleichung aller Resultate bei der konstanten Temperatur von 20° keine andere Begrundung als unsere Bequemlichkeit hat. Der Grundsatz wird allgemein anerkannt daß die physikalischen Eigenschaften einer Substanz bei solchen Temperaturen verglichen werden mussen daß das Verhaltnis

$$\frac{\text{Abs Vergleichstemperatur}}{\text{Abs kritische Temperatur}}$$

fur die verglichenen Substanzen konstant bleibt Wie sehr wir gegen diesen Grundsatz bei der Behandlung der Frage der optischen Aktivitat verstoßen braucht nicht weiter erklart zu werden

Dieser theoretische Rat laßt sich aber leider nicht leicht in die Praxis umsetzen denn die kritischen Konstanten sind fur nur wenige optisch aktive Substanzen bekannt und in manchem Falle uberhaupt nicht feststellbar

Patterson (Journ. Chem Soc 85 771 (1904)) schlug einen neuen Weg zur Umgehung dieser Schwierigkeit ein Es gibt wahrscheinlich fur jede optisch-aktive Substanz eine Temperatur bei welcher sie inaktiv ist Im Falle der flussigen optisch aktiven Substanzen kann

man durch Zeichnung einer Rotation Temperaturkurve die Temperatur der Inaktivitat feststellen Patterson hat dies fur die Dimethyl-, Diathyl und Di n propylester der d Weinsaure getan und gefunden, daß die Aktivitat des Dimethylesters bei 0°, des Diathyl esters bei — 34°, des Di n propylesters bei — 60° verschwindet Er nimmt an, daß die Ester sich bei diesen Temperaturen und bei gleichen Intervallen von diesen Temperaturen, also bei t, (t — 34) und (t — 60) in einem gleichen optischen Zustand befinden, und daher vergleichbare Zahlen geben mussen Er vergleicht also die molekulare Drehung dieser drei Ester für verschiedene vergleichbare Temperaturen zwischen 0° und 120° und konstatiert, daß in der Tat ein deutlicher quantitativer Zusammenhang zwischen den Resultaten hervortritt, was nicht der Fall war wenn er die molekularen Drehungen bei derselben Temperatur verglich

Experimenteller Teil

A 1) Darstellung von Homothujylalkohol

Bekanntlich kann man homologe Alkohole sehr gut nach der Grignard schen Methode durch Einwirkung von Alkyl Magnesiumjodid auf Ketone darstellen Um sicher einen Uberschuß von Methyl Magnesiumjodid zu haben wurden zwei Molekule Magnesium und zwei Molekule Methyljodid auf ein Molekul Thujon verwendet Der verwendete Ather war uber Natriumdraht getrocknet aber sonst nicht gereinigt worden Um aus dem Reaktionsgemisch den gebildeten Alkohol zu gewinnen wurden zwei verschiedene Methoden angewandt Erstens wurde das Reaktionsgemisch in kleinen Mengen unter Umschutteln auf reines Eis gegossen und mit Essigsaure angesauert bis samtliches Magnesium hydroxyd gelost war Alsdann wurde der Alkohol durch Ausathern gewonnen Zweitens Nachdem das Reaktionsgemisch auf reines Eis gegossen war wurde es einer Wasserdampfdestillation unterworfen und der entstandene Alkohol dann aus dem Destillat durch Ausathern gewonnen Die atherische Losung wurde uber geschmolzener Pottasche getrocknet der Ather abgedampft und alsdann bei gewohnlichem Drucke weiter destilliert Das von 202° bis 206 aufgefangene Destillat

wurde in einer Kaltemischung gründlich abgekühlt Ein Teil des Öls krystallisierte sofort aus Dieser Teil wurde abgesaugt, auf Ton abgepreßt und aus Methylalkohol umkrystallisiert Smp 84° Die Ausbeute an gereinigtem festen Homothujylalkohol war nie mehr als 12 % bis 15 % der angewendeten Menge Thujon Das Filtrat war ein hellgelbes Öl vom Sdp 202—205, das nicht zum Krystallisieren gebracht werden konnte

Analyse des festen Homothujylalkohols

0 2295 g Substanz gaben 0 6600 g CO_2 0,2482 g H_2O
Berechnet für $C_{11}H_{22}O$ C = 78,49 % H = 12,01 %
Gefunden C = 78 42 % H = 12,13 %

Drehung des festen Homothujylalkohols

I S = 0,8027 g L (Äther) = 19 7764 p = 4,058
t = 15° d = 0,728 l = 2,2 dm α_D = −1,93
$[\alpha]_D$ = −30,0

II S = 1 7900 g L (Äther) = 21,4376 p = 8,350
t = 13° d = 0,739 l = 2,2 dm α_D = −3,93
$[\alpha]_D$ = −28,9

III S = 0 8625 g L (Methylalkohol) = 20 5822 p = 4,191
t = 12° d = 0 8055 l = 2,2 dm α_D = −1,93
$[\alpha]_D$ = −26,0

Drehung des flüssigen Alkohols Sdp 202—203

I S = 1,0486 L (Äther) = 20,0635 p = 5,226
t = 15° d = 0,731 l = 2 2 dm α_D = +3,016
$[\alpha]_D$ = +35,9

II S = 2 0603 L (Äther) = 20 0984 p = 10 25
t = 15° d = 0 7430 l = 2 2 dm α_D = +5 88
$[\alpha]_D$ = +35 1

Verschiedene Versuche ein Semicarbazon aus dem Öl darzustellen schlugen fehl Daher ist die Abwesenheit von unangegriffenem Thujon erwiesen Der einzig mögliche Schluß ist daß zwei stereoisomere Alkohole vorliegen ein fester und ein flüssiger

Es wurde versucht, auf drei verschiedenen Wegen beide Alkohole näher zu charakterisieren

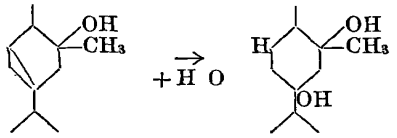
1 Darstellung der entsprechenden Urethane
2 Hydratation
3 Wasserabspaltung

A 2) Versuch die Urethane darzustellen

Weder der flüssige noch der feste Alkohol bildet ein Urethan wenn man ihn in der üblichen Weise mit Phenylisocyanat behandelt

A 3) Hydratationsversuch

Es war möglich daß beide tertiäre Alkohole mit einer fünfprozentigen Schwefelsäurelösung geschüttelt nach dem folgenden Schema Wasser addieren würden



Dabei müßten voraussichtlich der feste und der flüssige Alkohol verschiedene Glykole liefern

Es wurde also ein Gramm des festen tertiären Alkohols in 500 ccm fünfprozentiger Schwefelsäure suspendiert und drei Wochen auf der Schüttelmaschine geschüttelt Das erhaltene Produkt wurde mit Natronlauge neutralisiert und zehn Minuten lang mit Wasser

dampf destilliert, um unangegriffenen Alkohol zu entfernen Fast die ganze Menge des Alkohols wurde unverandert zuruckgewonnen Der abgekuhlte Ruckstand wurde mit Essigather grundlich ausgezogen Nach dem Abdampfen des Essigathers hinterblieben nur Spuren eines Ols, das trotz langen Stehens nicht fest wurde

5 g des flussigen Alkohols wurden zwei Wochen lang mit 1000 ccm funfprozentiger Schwefelsaure geschuttelt Ich erhielt bei der gleichen Verarbeitung ein gleiches Resultat, denn auch hier wieder ging fast der ganze Alkohol bei der Wasserdampfdestillation unangegriffen uber

Der Schluß ist berechtigt daß der innere Ring bei beiden Alkoholen gerade wie beim Thujylalkohol gegen verdunnte Schwefelsaure bestandig ist

Vgl hierzu Wallach Ann **360**, 84—86 und Wallach „Terpene und Campher" S 60

A 4) Wasserabspaltungsversuche

Ein Gramm des festen Homothujylalkohols wurde mit zwei Gramm pulverisiertem wasserfreien Kalium bisulfat gemischt und eine Stunde lang am Ruckfluß kuhler bei ungefahr 150° erhitzt Nachdem das Reaktionsgemisch sich abgekuhlt hatte, wurde Wasser zugesetzt, bis das Kaliumbisulfat gelost war Die Losung wurde alsdann schwach alkalisch gemacht Die alkalische Losung wurde mit Wasserdampf behandelt und dabei ein oliges Destillat gewonnen Der ungesattigte Charakter des Ols ergibt sich durch seine Fahigkeit, *momentan Kaliumpermanganatlosung* zu entfarben, wahrend der ursprungliche Alkohol nicht mit Kaliumpermanganat reagiert Beim Versuch, daraus

ein Nitrosylchlorid darzustellen erhielt ich ein Öl dessen weitere Untersuchung erfolglos schien

Die mittels H_2SO_4 erhaltenen Wasserabspaltungsprodukte sowohl vom festen wie auch vom flüssigen Alkohol gaben ein ähnlich unbefriedigendes Ergebnis Auch die Bromierungsprodukte waren öl ig

A 5) Darstellung und Drehung von Thujylalkohol

36 g Thujon wurden mit der berechneten Menge Natrium und Alkohol reduziert nach der Vorschrift von Semmler (Ber 25 3344 (1892)) Der in vorzüglicher Ausbeute entstandene Thujylalkohol wurde zweimal destilliert Sdp 212—213°

Drehung des Thujylalkohols

I S = 1 0547 g L (Äther) = 19 3446 p = 5 4502
t = 14° d = 0 7352 l = 2 2 dm α_D = +4 99
$[\alpha]_D$ = +56 6

II S = 2 1542 g L (Äther) = 21 5415 p = 10 00
t = 14° d = 0 7431 l = 2 2 dm α_D = +9 15
$[\alpha]_D$ = +55 9

III S = 0 9804 L (Methylalkohol) = 21 2487 p = 4 614
t = 13° d = 0 8053 l = 2 2 dm α_D = +4 28
$[\alpha]_D$ = +52 3

A 6) Darstellung von tertiären Äthyl n Propyl und Isopropyl Thujylalkoholen

Diese Alkohole wurden mittels der Grignardschen Reaktion nach dem gewöhnlichen Verfahren dargestellt Das verwendete Thujon siedete bei 81—82 unter 10—12 mm Druck $[\alpha]_D$ = +67 4 In jedem Falle entstanden Flüssigkeiten die keinen scharfen Siedepunkt besaßen Beim Abkühlen in einer Kältemischung schied

sich keine feste Substanz aus Da die Ole auch hier nicht mit Semicarbazid reagierten ist die Abwesenheit von unangegriffenem Thujon bewiesen Diese hoheren Homologen der beiden isomeren Methylthujylalkohole sind also Flussigkeiten, deren Trennung jetzt nicht moglich erscheint

Im Folgenden die Zahlenangaben

Athylthujylalkohol Sdp_{8-9} 91—94

Analyse 0 2015 g Substanz gaben 0 5852 g CO und 0,2180 g HO_2

Berechnet fur $C_1 H_{22} O$ C = 79,03 % H = 12,19 %

Gefunden C = 79,20 „ H = 12,13 „

Drehung

I t = 15° d = 0,9193 l = 1 dm α_D = +53,92

$[\alpha]_D$ = +58,7

II S = 0,9825 L (Methylalkohol) = 19,8240 p = 4,956

t = 16° d = 0,8037 l = 2,2 dm α_D = +5,38

$[\alpha]_D$ = +61,4

Propylthujylalkohol Sdp_{23} = 91 – 103

Drehung

S = 0,7200 L (Methyl Alkohol) = 18 8716 p = 3,815

t = 13° d = 0 8034 l = 2,2 dm α_D = +3,88

$[\alpha]_D$ = +57,5

A 7) Darstellung des Benzylidenthujons

$C_{10} H_{14} O$ CH $C_6 H_5$

Diese Verbindung wurde mittels Kondensation von Benzaldehyd und Thujon gewonnen Es wurde genau nach Semmlers Vorschrift (Ber 36, 4367) verfahren Das in vorzuglicher Ausbeute erhaltene Produkt wurde zweimal destilliert

Sdp $_{-3}$ = 176—179
Vgl Semmler l c Sdp$_9$ = 178
Haller (C r **140** 1626 (1905)) Sdp$_{12}$ = 176—178

Drehung

S = 0 9862 L (Methylalkohol) = 9 0459 p = 10 902
t = 17° d = 0 818 l = 1 dm α_D = − 52 716
$[\alpha]_D$ = − 591

vgl Haller l c $[\alpha]_D$ = − 590 8 (c = 2 9505 in Athyl alkohol)

A 8) Darstellung des Oxymethylenthujons

$C_{10}H_{14}O$ CHOH

Diese Verbindung wurde nach der Wallachschen Modifikation der Claisenschen Methode hergestellt (Vgl Steindorff Diss Gottingen 1903 und Wallach Ber 28 33 (1895)) Ein Molekul Thujon und ein Molekul Amylformiat wurde in etwa funffacher Menge trockenen Athers aufgelost und die entsprechende Menge (1 Mol) fein geschnittenes Natrium hinzugesetzt Die Reaktion tritt bei Zimmertemperatur sofort ein Ein zu stur mischer Verlauf wird durch gelegentliches Abkuhlen verhindert Wenn samtliches Natrium verbraucht ist athert man aus um unangegriffenes Thujon mit an deren Verunreinigungen zu entfernen Alsdann wird die Oxymethylenverbindung mit 30 %iger Essigsaure ge fallt in Ather aufgenommen und uber Chlorcalcium ge trocknet

Sdp $_5$ = 114—116
Vgl Wallach (Ber 28 33 (1895)) Sdp $_6$ = 115—118

Drehung des Oxymethylenthujons

I Frisch dargestellt

$t = 19^0$ $d = 1{,}022$ $l = 1$ dm $\alpha_D = -12\,16$

nach 48 Stunden $\alpha_D = -10\,566$

(konstant)

$[\alpha]_D = -10{,}34$

II S = 0,5264 L (Methylalkohol) = 9,5092 p = 5,5358

$t = 18^0$ $d = 0{,}8055$ $l = 1$ dm $\alpha_D = -0{,}45$

$[\alpha]_D = -10{,}1$

B 1) Darstellung von α Thujaketosaure aus Thujon

Wenn man Thujon mit verdunnter Kaliumperman ganatlosung behandelt, wird es zur entsprechenden Ketosaure (Wallach, Ann **272**, 113) (S S 18)

Nach mehreren Versuchen hielt ich folgende Me thode, die mir die beste Ausbeute ergab, ein In einer geraumigen Flasche wurde zu rohem Thujon ($\alpha_D = +64\,0$) zerkleinertes Eis gegeben und die be rechnete Menge (2 Atome O) einer 5 %igen Kalium permanganatlosung zugesetzt Die Flasche wurde als dann auf die Schuttelmaschine gebracht und nach wenigen Stunden trat Entfarbung ein Die Flussigkeit wurde von abgeschiedenem Mangandioxyd abgesaugt und auf dem Wasserbade bis zum Beginn einer Hautbil dung auf der Oberflache eingedampft Gewohnlich bleibt unangegriffenes Thujon beim Filtrieren zuruck Sollten Oltropfen auf dem klaren Filtrat schwimmen bleiben, so kann man sie mittelst eines Scheidetrichters leicht ab trennen Um eine schadliche Einwirl ung des Alkalis beim Eindampfen zu verhuten stumpfte ich es durch Zusatz von kleinen Mengen Schwefliger Saure ab, ohne

völlig anzusäuren Die Flüssigkeit wurde nun filtriert abgekühlt und mit verdünnter Schwefelsäure angesäuert Hat man nicht zu weit eingedampft so pflegt sich die α Thujaketosäure sofort in fester Form abzuscheiden Falls zu weit eingedampft worden ist oder Verunreinigungen anwesend sind scheidet sich ein Öl ab das gewöhnlich nach kurzem Stehen fest wird Die letzten Reste der α Thujaketosäure können durch Ausäthern gewonnen werden Die Säure krystallisiert aus siedendem Wasser in Blättchen aus Smp 75—76 Nach mehrmaligem Waschen mit kaltem Wasser und Pressen auf Tonteller kann gewöhnlich die rohe Säure ohne weiteres zur Darstellung der α Dicarbonsäure verwendet werden

Die Entstehung von β Säure neben der α Säure wurde nicht bemerkt

Ausbeute 75 g rohes Thujon gaben 45—50 g Thujaketosäure

Drehung der α Thujaketosäure

I S = 0 9859 L (Äther) = 14 1978 p = 6 945
t = 14 d = 0 742 l = 2 2 dm α_D = + 22 00
$[\alpha]_D$ = + 194

II S = 0 5776 L (Eisessig) = 12 5122 p = 4 6163
t = 19° d = 1 0524 l = 1 dm α_D = + 10 886
$[\alpha]_D$ = + 224 1

III S = 0 4843 L (Methylalkohol) = 8 7026 p = 5 5649
t = 19° d = 0 8064 l = 1 dm α_D = + 9 64
$[\alpha]_D$ = + 214 8

IV S = 0 5669 L (Chloroform) = 14 1646 p = 4 0093
t = 15° d = 1 467 l = 1 dm α_D = + 14 31
$[\alpha]_D$ = + 243 7

V S = 0,7298 L (Chloroform) = 14,2209 p = 5,132
t = 16° d = 1,458 l = 2 2 dm α_D = + 18 313
$[\alpha]_D$ = + 244 8

VI S = 0,1566 L (Wasser) = 23,185 3 p = 0,675 4
t = 18° d = 1 002 l = 2,2 dm α_D = + 3,633
$[\alpha]_D$ = + 244 0

Drehung des Ammoniumsalzes der α Thujaketosäure

S = 0,2591 L (Wasser) = 29,415 p = 0,881
t = 19° d = 1 007 l = 2,2 dm α_D = + 3,333
$[\alpha]_D$ = + 170

b 2) Darstellung des Semicarbazons der α Thujaketosäure

3 g α Thujaketosäure wurden in Eisessig gelöst Dieser Lösung wurde eine wässerige Lösung der berechneten Menge Semicarbazidchlorhydrat und Natriumacetat zugesetzt Das Semicarbazon krystallisierte nach einigen Minuten aus Es wurde aus Eisessig umkrystallisiert

Kurze weiße Nadeln vom Smp 183—184
Ausbeute (rohe Substanz) = 3,8 g

Drehung

S = 0 6062 L (Eisessig) = 26 4854 p = 2 290
t = 16 d = 1,0605 l = 2 2 dm α_D = + 12,17
$[\alpha]_D$ = + 227 8

Die obige Lösung war bei Zimmertemperatur gesättigt Das Semicarbazon ist noch weniger löslich in Methylalkohol Eine methylalkoholische Lösung (p = 1,473), durch kurzes Erwärmen hergestellt, schied im

Beobachtungsrohr Krystalle ab Die übrige Flüssigkeit zeigte eine Drehung von

$$\alpha_D = +10\,00$$
$$[\alpha]_D = \text{ca. } +380$$

B 3) Darstellung und Drehung des Oxims der α Thujaketosäure

Diese Verbindung wurde in alkalischer so wie auch in neutraler Lösung dargestellt die so erhaltenen Oxime waren sowohl dem Schmelzpunkte als auch der Drehung nach verschieden Das Verfahren in alkalischer Lösung war genau der Vorschrift von Lazell (Diss Göttingen 1896 S 26) entsprechend und das erhaltene Oxim schmolz nach der Umkristallisation aus Methylalkohol bei 169—170 also in guter Übereinstimmung mit Lazells Angabe 168

Drehung

S = 0 8031 L (Methylalkohol) 20 4254 p = 3 933
t = 15 d = 0 8083 l = 2 2 dm $\alpha_D = -0\,35$
$[\alpha]_D = -5\,00$

Die Darstellungsweise in neutraler Lösung war die folgende

2 2 g Hydroxylaminchlorhydrat in möglichst wenig Wasser gelöst wurden einer methylalkoholischen Lösung der berechneten Menge Natriummethylat (0 77 g Natrium in 16 ccm Methylalkohol) zugesetzt Nachdem vom ausgeschiedenen Chlornatrium abfiltriert war wurde zu dem klaren Filtrate eine warme Lösung von 3 g α Thujaketosäure in Methylalkohol gegeben Das Gemisch wurde am Rückflußkühler 2—3 Stunden auf dem Wasserbade gekocht Nachher wurde der überschüssige Methylalkohol mit Wasserdampf abgeblasen Ungefähr die Hälfte an Oxim schied sich sofort in dem Kolben

aus Der übrige Teil wurde aus der gut gekühlten Flüssigkeit durch Ansäuern mit verdünnter Essigsäure erhalten Smp (aus Methylalkohol) = 174—175, also 5 Grad höher als das Oxim aus der alkalischen Lösung

Drehung des Oxims (Smp 174—175)

I Eine Lösung p = 4,473 im Methylalkohol gab keine meßbare Drehung

II S = 0 1600 L (Eisessig) = 9,4072 p = 1,7008
t = 14° d = 1,058 l = 1 dm α_D = +0,10
$[\alpha]_D$ = +5,56

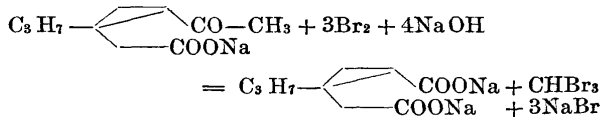
III In verdünnter Natronlauge dreht stark links

C 1) Darstellung der α Dicarbonsäure (Tanaceton dicarbonsäure)

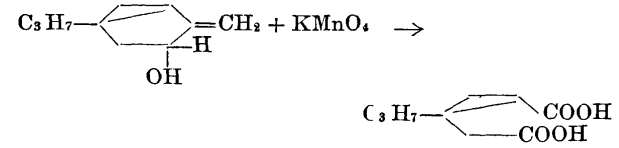
Diese Säure läßt sich nach zwei Methoden darstellen

Erstens durch Oxydation der α Thujaketosäure mit Natriumhypobromit nach Semmler (Ber **25** 3348)

Zweitens durch direkte Oxydation des Sabinols mit Kaliumpermanganat nach Fromm (Ber **31**, 2030) Im ersten Falle haben wir folgende Reaktionsgleichung



Im zweiten Falle verläuft die Reaktion folgendermaßen



Auf Grund einiger Erfahrung läßt sich nach beiden Methoden eine fast theoretische Ausbeute erzielen Der größte Teil der bei den folgenden Experimenten verwendeten α Dicarbonsäure wurde aus α Thujaketosäure dargestellt Da Semmlers Angaben zur Erzielung einer guten Ausbeute nicht ausreichend sind lasse ich die genaue Beschreibung der Darstellungsmethode dieser wichtigen Säure folgen

20 g pulverisierte α Thujaketosäure werden in einer Flasche durch möglichst wenig 4 %ige Natronlauge unter gelindem Erwärmen auf dem Wasserbade in Lösung gebracht Die verwendete α Thujaketosäure muß ziemlich rein sein Wenn sie nach dem oben beschriebenen Verfahren dargestellt wird kann man die so erhaltene rohe Säure ohne weiteres für diesen Zweck verwenden Zur warmen alkalischen Lösung der Säure werden kleine Mengen (10—20 ccm) einer Lösung von der berechneten Menge Brom (6 Atome = 51 7 g) in etwa 700 ccm 4 %iger Natronlauge unter jedesmaligem Umschütteln zugesetzt Die Hypobromitlösung muß eine ausgeprägt gelbe Farbe haben Falls die Farbe der Lösung rot oder braun ist muß man solange Natronlauge zusetzen bis sie gelb geworden ist Die Oxydation tritt gewöhnlich sofort ein und läßt sich an dem Verschwinden der gelben Farbe und dem Auftreten einer milchweißen Trübung (Ausscheidung von Bromoform) erkennen Nachdem die ganze Hypobromitlösung zugesetzt worden ist läßt man das Reaktionsgefäß etwa eine halbe Stunde stehen damit sich sämtliches Bromoform abscheiden kann Die ganze Oxydation läßt sich bei einer Temperatur von 30—40° in wenigen Minuten ausführen Die klar gewordene Flüssigkeit wird dekantiert und auf dem Wasserbade bis zum Anfang der Krystalli

sation oder Hautbildung an der Oberflache eingeengt Vor dem Eindampfen mussen der Losung einige Tropfen einer Losung von Natriumbisulfit zugesetzt werden, falls beim Ansauren einer Probe der Losung freies Brom (aus NaBrO) entsteht Die eingeengte Flussigkeit wird alsdann filtriert, gut abgekuhlt und mit verdunnter Schwefelsaure unter stetem Umruhren angesauert Hat man nicht zu stark eingedampft, so scheidet sich die Dicarbonsaure sofort in fester, krystallinischer Form aus Nach kurzem Stehen wird der Niederschlag abgesaugt und aus kochendem Wasser umkrystallisiert Die letzten Ruckstande an Dicarbonsaure konnen aus den Filtraten durch Ausathern gewonnen werden

Ausbeute Aus 20 g α Thujaketosaure erhielt ich 19,5 g Dicarbonsaure, die ohne weiteres bei 139—140 schmolz Nach einmaligem Umkrystallisieren aus kochendem Wasser war der Smp 141—142

Die Oxydation laßt sich auch gut und ohne Ringverschiebung mit konzentrierterer Natronlauge anstellen, aber dann wird die gewonnene Saure leicht mit mehr oder weniger Natriumsulfat verunreinigt Die Dicarbonsaure ist, im Gegensatz zu der α Thujaketosaure, in Petrolather so gut wie unloslich

Drehung der α Dicarbonsaure

I S = 0,8470 L (Ather) = 16 9670 p = 4,991
t = 15° d = 0,734 l = 2,2 dm α_D = + 8,47
$[\alpha]_D$ = + 105,1

II S = 0,6318 L (Eisessig) = 12,8476 p = 4,9177
t = 18° d = 1,0586 l = 1 dm α_D = + 6,933
$[\alpha]_D$ = + 133,2

III S = 0 8278 (Chloroform) = 28 818? p = 2 8726
t = 15 d = 1 480 l = 1 dm α_D = + 7 29
$[\alpha]_D$ = + 171 5

IV S = 0 5378 I (Methylalkohol) = 11 4322 p = 4 7043
t = 16° d = 0 810 l = 1 dm α_D = + 3 96
$[\alpha]_D$ = + 104

V S = 0 1716 L (Wasser) = 23 4346 p = 0 7393
t = 18° d = 1 003 l = 2 9 dm α_D = + 2 183
$[\alpha]_D$ = + 135 1

C 2) Saures und normales Ammoniumsalz der α Dicarbonsäure

Um die Drehung des α Dicarbonsäuremonamids die später beschrieben wird mit der des sauren und normalen Ammoniumsalzes der α Dicarbonsäure vergleichen zu können wurden die beiden letzteren dargestellt Die Lösung des sauren Ammoniumsalzes wurde durch Mischung von Dicarbonsäure und Ammoniumcarbonat (Hirschhornsalz) im Verhältnis von 1 Mol Säure zu ½ Mol Hirschhornsalz dargestellt Das normale Ammoniumsalz erhielt ich durch gelindes Eindampfen einer Lösung von Dicarbonsäure in Ammoniak

Drehung des sauren Ammoniumsalzes
S = 0 2441 L (Wasser) = 30 766 p = 0 793
t = 17° d = 1 005 l = 2 2 dm α_D = + 0 266
$[\alpha]_D$ = + 15 2

Drehung des normalen Ammoniumsalzes
S = 0 4330 L (Wasser) = 11 3794 p = 3 805
t = 18° d = 1 0105 l = 2 2 dm α_D = − 0 453
$[\alpha]_D$ = − 5 3

Die Drehung ändert sich ziemlich schnell mit der

Verdunnung Die obige Losung mit dem gleichen Volum Wasser verdunnt zeigte $\alpha_D = -0{,}30$, $[\alpha]_D = -7{,}1$

C 3) Darstellung des Anhydrids der α Dicarbonsäure

Das Anhydrid wurde nach Semmler (Ber 25, 3349) erhalten

Weiße Nadeln vom Smp 56

Das Anhydrid laßt sich leicht durch Kochen mit verdunnter Salzsaure in die ursprungliche α Dicarbonsaure zuruckverwandeln

Drehung des Anhydrids

S = 0 2791 L (Ather) = 6,8586 p = 4 069
t = 17° d = 0 730 l = 1 dm α_D = + 0 30
$[\alpha]_D$ = + 10,1

S = 0 3409 L (Chloroform) = 12,9034 p = 2,642
t = 13° d = 1,481 l = 1 dm α_D = + 0,33
$[\alpha]_D$ = + 8,43

C 4) Darstellung des α Dicarbonsäuremonamids aus dem Anhydrid der α Dicarbonsaure

Diese Substanz ist durchaus nicht einfach darzustellen, da sie leicht eine klebrige Schmiere bildet Nach vielen Versuchen wurde die folgende Methode ausgearbeitet

Funf Gramm reines α Dicarbonsaureanhydrid wurden in so wenig wie moglich warmem absoluten Alkohol gelost und unter Abkuhlung getrocknetes Ammoniakgas bis zur Sattigung eingeleitet Wird die gesattigte Losung an der Luft stehen gelassen, dann scheidet sich langsam eine feste Substanz ab, die sich als das Ammoniumsalz des α Dicarbonsauremonamids erwies Es wurde abfiltriert, auf Ton getrocknet, in so wenig wie

moglich Wasser gelost und alsdann mit verdunnter Salzsaure tropfenweise angesauert Entweder sofort oder nach einigem Stehen scheiden sich die feinen weißen wohlausgepragten Krystalle des Monamids ab Sie werden abfiltriert und dadurch gereinigt daß man sie in moglichst wenig verdunntem Ammoniak lost und wieder mit verdunnter Salzsaure ausfallt Die so erhaltenen Krystalle erwiesen sich mit Wasser gut ausgewaschen und auf Ton getrocknet als halogenfrei und stickstoffhaltig Sie sind bei Zimmertemperatur in Wasser Ather und Chloroform fast unloslich in Methylalkohol schwerloslich

Smp 149—150 also 8 Grad hoher als die α Dicarbonsaure

Analyse

0 1796 g Substanz gaben 0 3844 g CO_2 0 1318 g H_2O

Berechnet fur

$C_9H_{15}O_3N$ C = 58 34 % H = 8 167 %

Gefunden C = 58 37 % H = 8 209 %

Drehung

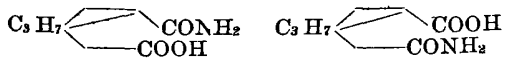
S = 0 2980 g L (Methylalkohol) = 7 8902 p = 3 777

t = 15 d = 0 8084 l = 1 dm α_D = + 1 666

$[\alpha]_D$ = + 54 5

Nach drei Stunden unverandert

Welche der beiden moglichen Formeln



die erhaltene Verbindung darstellt ist noch nicht fest gestellt worden

Ammoniumsalz des Monamids der α-Dicarbonsaure

Diese Verbindung wurde wie oben beschrieben, durch Einleiten von getrocknetem Ammoniakgas in eine Losung von Dicarbonsaureanhydrid in absolutem Alkohol dargestellt Sie wurde aus warmem absolutem Alkohol umkrystallisiert

Analyse
0,1813 g Substanz gaben 0 3637 g CO_2, 0 1473 g H O
Berechnet fur
$C_9H_{18}O_3N_2$ C = 53 42 % H = 8 973 %
Gefunden C = 54 71 % H = 9 088 %

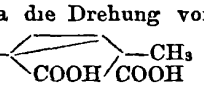
Die Analyse zeigt daß der verwendeten Substanz Spuren von freier Monamidosaure beigemengt waren die sich wohl durch Hydrolyse beim Umkrystallisieren gebildet hatten

I S = 0 1670 L (Wasser) = 9 7498 p = 1,713
t = 17 d = 1 006 l = 2 2 dm α_D = −0,666
$[\alpha]_D$ = −17,6
II S = 0 3795 L (Methylalkohol) = 8 0850 p = 4,694
t = 18° d = 0 808 l = 1 dm α_D = +0 35
$[\alpha]_D$ = +9,2

C) a) Versuch aus dem Anhydrid der α Dicarbonsaure die entsprechende Anil und Piperidilsaure darzustellen

Das Dicarbonsaureanhydrid reagiert leicht mit Anilin und Piperidin (1 Mol) unter betrachtlicher Warmeentwicklung Das Produkt der Addition von Anilin ist ein nicht krystallisierendes Glas, das von Piperidin eine Flussigkeit

D Versuch Homotanacetondicarbonsäure aus Benzyliden und Oxymethylenthujon darzustellen

Da die Drehung von Homotanacetondicarbonsaure C_3H_7—  —CH_3 und dessen Anhydrid noch nicht bestimmt sind wurden zwei Versuche gemacht diese Saure durch Oxydation von Benzyliden Tanaceton $C_{10}H_{14}O$ CH C_6H_5 mit Kaliumpermanganat (4 Atome O) nach Semmler s Vorschrift (Ber 36 4367 (1903)) darzustellen Obwohl diese Vorschrift mit der peinlichsten Genauigkeit befolgt wurde war das Resultat bei beiden Versuchen identisch Es wurde jedesmal eine olige Schmiere erhalten die trotz aller Bemuhungen nicht zur Krystallisation gebracht werden konnte Daß dieser Mißerfolg nicht in dem verwendeten Benzyliden Tanaceton lag geht klar aus seinen Konstanten hervor

Zwei Versuche durch Oxydation des Oxymethylenthujons $C_{10}H_{14}O$ CH OH mit Kaliumpermanganat diese Saure darzustellen gaben dasselbe unbefriedigende Resultat

E 1) Beständigkeit des Dreirings in α Thujaketosäure

10 g α Thujaketosaure wurden mit 1000 ccm 20 %iger Salzsaure zwei Stunden lang gekocht Die Flussigkeit wurde alsdann 15 Minuten lang einer Wasserdampfdestillation unterworfen Es ging ein Ol von angenehmem Geruch des Hydropseudocumols uber das sich als ungesattigt erwies Uber Natrium destilliert siedete es von 160—165° (Vgl Hydropseudocumol Sdp 160)

Der flussige Ruckstand wurde gut ausgeathert Nach Abdestillation des Athers hinterblieb ein saures Ol, das optisch inaktiv war und nach tagelangem Stehen nicht fest wurde

Der Dreiring in der α Thujaketosaure ist also gegen heiße verdunnte Salzsaure nicht bestandig

E 2) Beständigkeit des Dreirings in der α Dicarbon saure (Tanacetondicarbonsaure) gegen verdunnte Salzsaure und Natronlauge

Ein halbes Gramm Dicarbonsaure wurde mit 100 ccm ca 20 % iger Salzsaure zwei Stunden lang am Ruckfluß kuhler gekocht und die saure Losung alsdann auf dem Wasserbade zur Trockne eingedampft

Smp (unverandert) = 141—142
$[\alpha]_D$ (p = 2 703 in Ather) = + 109

Reine Substanz $[\alpha]_D$ (p = 4,991 in Ather) = + 105

Es folgt daraus daß der Dreiring in der α Dicar bonsaure gegen verdunnte Salzsaure selbst in der Siede hitze sehr bestandig ist

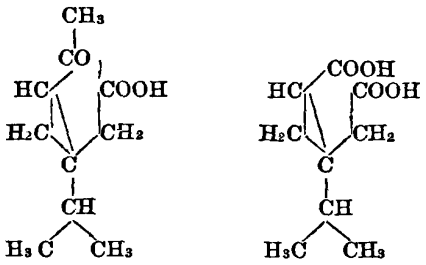
1 g α Dicarbonsaure wurde in 100 ccm 10 % iger Natronlauge anderthalb Stunden am Ruckflußkuhler ge kocht Die erkaltete Losung wurde mit Salzsaure an gesauert und mit Ather ausgezogen Die so erhaltene Saure schmolz ohne weiteres zwischen 138—139 (Reine Substanz Smp 141—142) und zeigte die spezifische Drehung

$[\alpha]_D$ = + 101 (p = 7,296 in Ather)
(Reine Substanz) $[\alpha]_D$ = + 105 (p = 4 991 „ „)

Man sieht also, daß der Dreiring in der α Dicar

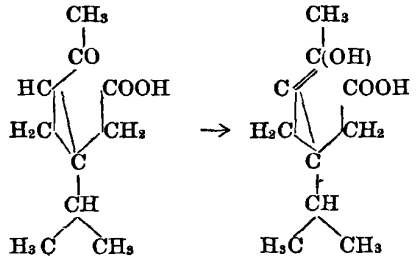
bonsaure auch gegen kochende verdunnte Natronlauge bestandig ist

Die ganz verschiedene Festigkeit des Dreiring systems in der α Thujaketonsäure einerseits und in der aus ihr durch Oxydation gewonnenen α Dicarbonsaure anderseits ist sehr beachtenswert



sehr labil sehr stabil

Ahnliches findet man bei der Pinon und Pinsaure Wallach schreibt die Unbestandigkeit der Ketoform einer Enolisierung zu die die Entstehung eines quaternar gebundenen Kohlenstoffatoms ermoglicht z B



1) A 300 85 Vgl au h B h er Ann 84 198 (189) nd K t u d Stalma n J u p akt Chem ( ) 68 1 (1903)

F 1) Versuch, den Methylester der α Thujaketo saure darzustellen

10 g sorgfaltig gereinigte α Thujaketosaure wurden in so wenig wie moglich Ammoniak gelost -Zu dieser Losung wurde eine klare Losung von Silbernitrat in geringem Uberschuß zugesetzt Das abgeschiedene Silbersalz wurde mit Wasser gut ausgewaschen und auf Ton in einem braunen Glasexsiccator getrocknet Es wurde alsdann in einer Reibschale mit Methylalkohol verrieben und in einen Rundkolben hineingespult Eine Losung von Methyljodid (doppelte berechnete Menge) wurde hinzugesetzt Unter gutem Umschutteln wurde das Gemisch am Ruckflußkuhler auf dem Wasserbade eine Stunde lang gekocht Die stattgefundene Esteri fikation wurde durch reichliches Abscheiden von Silber jodid angezeigt Nach dem Abdestillieren vom Methyl alkohol und uberschussigem Methyljodid hinterblieb ein Ol, das sich bei der Vakuumdestillation zersetzte

F 2) Esterifikation der α Dicarbonsäure

In allen Fallen war die Methode der Esterifikation folgende Eine abgewogene Menge (5—20 g) der reinen α Dicarbonsaure wurde in dem Drei bis Vierfachen der berechneten Menge des betreffenden reinen Alkohols in einem Destillationskolben gelost Es wurde trockener Chlorwasserstoff in die Losung bis zur Sattigung (5—6 Stunden) eingeleitet Der Kolben wurde dann fest ver schlossen und 12—24 Stunden lang stehen gelassen Darauf wurde in vacuo destilliert Nachdem der uber schussige Alkohol und Chlorwasserstoff entfernt waren, ging der Ester uber Er wurde durch wiederholte Destillation in vacuo weiter gereinigt bis eine konstant

siedende und drehende Fraktion erzielt war Auf diese Weise wurden der Dimethyl Diathyl Di n propyl Diisobutyl Diisoamyl und Monobenzylester der α Dicarbonsaure dargestellt Die Esterifikation mit den drei ersten Alkoholen geht glatt mit den drei letzteren nicht so leicht

Samtliche Ester sind klare geruchlose mehr oder weniger zahe Flussigkeiten die auch bei starker Ab kuhlung nicht fest werden Mit Ausnahme des gelb gefarbten Monobenzylesters sind sie farblos

Verseifung der Ester und Untersuchung der Dre hung der erhaltenen Sauren wurden bei dem Methyl Athyl und Isoamylester ausgefuhrt In jedem Falle war die erhaltene Saure im Schmelzpunkte und in der Drehung identisch mit der angewandten α Dicarbon saure Dadurch ist bewiesen daß wahrend der Esteri fikation keine Racemisierung stattgefunden hat

Die Ester sind durchaus bestandige Verbindungen und geben bei Behandlung mit konzentrierter Ammoniak losung in keinem Falle ein Diamid

Dimethylester der α Dicarbonsaure

$C_7H_2(COOCH_3)_2$

Sdp_3 = 126—127 bei gewohnlichem Drucke 244—247

d_{20} = 1 0535

n_D = 1 4506

Mit Anilin zwei Stunden am Ruckflußkuhler ge kocht gibt er kein Anilid

Mit Natrium in atherischer Losung behandelt bildet er eine Natriumverbindung

Analyse

0 9153 g Ester gaben 0 4853 g CO_2 0 1684 g H_2O

Berechnet für $C_{11}H_{18}O_4$ C = 61 65 H = 8 472

Gefunden C = 61 47 H = 8 756

Drehung

I $t = 18^0$ $d = 1{,}054$ $l = 1$ dm $\alpha_D = +150\,18$

$[\alpha]_D = +142\,5$

Nach einem Monat unverandert

II $S = 0\,5392$ L (Ather) $= 11{,}3590$ $p = 4{,}748$

$t = 20^0$ $d = 0\,731$ $l = 1$ dm $\alpha_D = +4{,}933$

$[\alpha]_D = +142{,}1$

III $S = 0\,9430$ L (Ather) $= 8{,}6789$ $p = 10\,86$

$t = 20^0$ $d = 0\,7465$ $l = 1$ dm $\alpha_D = +11{,}65$

$[\alpha]_D = +139\,2$

Diathylester der α Dicarbonsaure

$C_7H_{12}(COOC_2H_5)_2$

$Sdp_{12\,13} = 138—140$

$d_{19} = 1{,}019$

$n_D =$

Mit Natrium in atherischer Losung behandelt gibt er eine Natriumverbindung

Analyse

0,2064 g Substanz gaben 0,4861 g CO_2, 0,1690 g H_2O

Berechnet fur $C_{13}H_{22}O_4$ C = 64 42, H = 9 157 %

Gefunden C = 64 23, H = 9,163 %

Drehung

I $t = 19^0$ $d = 1{,}019$ $l = 1$ dm $\alpha_D = +116\,27$

$[\alpha]_D = +114{,}1$

Nach $4^1/_2$ Monaten $[\alpha]_D = +114{,}3$

II $S = 0\,6558$ L (Ather) $= 12\,7707$ $p = 5\,135$

$t = 18^0$ $d = 0{,}731$ $l = 1$dm $\alpha_D = +4\,35$

$[\alpha]_D = +115\,9$

III $S = 0{,}8503$ L (Ather) $= 8\,4413$ $p = 10{,}073$

$t = 18^0$ $d = 0\,7437$ $l = 1$ dm $\alpha_D = +7{,}93$

$[\alpha]_D = +106$

Di n Propylester der α Dicarbonsaure

$C_7H_{12}(COOC_3H_7)_2$

$Sdp_{11\ 13} = 157—160$

$d_{16\ 16} = 0\ 9969$

Analyse

0 1664 g Substanz gaben 0 4039 g CO 0 1531 g H_2O

Berechnet fur $C_{15}H_{26}O_4$	Gefunden
C = 66 61 %	66 20 %
H = 9 699 %	10 29 %

Drehung

I t = 12 d = 0 9973 l = 1 dm α_D = + 84 50

$[\alpha]_D$ = + 84 7

II S = 0 5730 L (Ather) = 8 4432 p = 6 786

t = 17° d = 0 740 l = 1 dm α_D = + 4 28

$[\alpha]_D$ = + 8o 2

Diisobutylester der α Dicarbonsaure

$C_7H_{12}(COOC_4H_9)_2$

$Sdp_{12\ 4} = 174—176$

$d_{15} = 0\ 9908$

Analyse

0 1725 g Substanz gaben 0 4258 g CO_2 0 1502 g H O

Berechnet fur $C_{17}H_{30}O_4$ (normalen Ester)	fur $C_{13}H_{2}O_4$ (sauren Ester)	Gefunden
C = 68 45 %	64 42 %	67 32 %
H = 10 14 %	9 154 %	9 74 %

Wie die Resultate der Analyse zeigen ist das Vorhandensein von Spuren des sauren Esters nicht ausgeschlossen Die Anwesenheit von Spuren des Isobutylalkohols (C = 64 79 %) bietet auch eine Erklarung fur den niedrigen Kohlenstoffgehalt

Drehung

I $t = 12^0$ $d = 0\,991$ $l = 1$ dm $\alpha_D = +76\,92$

$[\alpha]_D = +77{,}62$

II $S = 0\,4927$ L (Ather) $= 8\,8348$ $p = 5\,577$

$t = 12^0$ $d = 0{,}7385$ $l = 1$ dm $\alpha_D = +2\,95$

$[\alpha]_D = +71{,}6$

III $S = 0{,}8903$ L (Ather) $= 6{,}4947$ $p = 13{,}709$

$t = 12^0$ $d = 0{,}7610$ $l = 1$ dm $\alpha_D = +7{,}616$

$[\alpha]_D = +73{,}0$

Diisoamylester der α Dicarbonsaure

$C_7H_{12}(COOC\,H_{11})_2$

(Drehung des verwendeten Amylalkohols

$(l = 1\text{ dm})\,\alpha_D = -1^0{,}1)$

$Sdp_{10\,12} = 187—190$

$d_{15} = 0{,}9924$

Analyse

0,2048 g Substanz gaben 0 5066 g CO_2, 0,1812 g H_2O

Berechnet fur $C_{19}H_{34}O_4$ (normalen Ester)	fur $C_{14}H_{24}O_4$ (sauren Ester)	Gefunden
C = 69,88 %	65 58	67 46 %
H = 10,50 %	9,443	9 897 %

Der Mangel an Kohlenstoff ist hier wieder auf das Vorhandensein von Spuren des sauren Esters oder des Isoamylalkohols zuruckfuhrbar

Drehung

I $t = 15^0$ $d = 0\,9924$ $l = 1$ dm $\alpha_D = +72\,95$

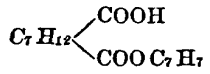
$[\alpha]_D = +73{,}5$

II $S = 0{,}5398$ L (Ather) $= 12{,}1813$ $p = 4\,4314$

$t = 16^0$ $d = 0{,}730$ $l = 1$ dm $\alpha_D = +2{,}366$

$[\alpha]_D = +73\,1$

Monobenzylester der α Dicarbonsaure



$Sdp_{12\ 14}$ = 210—220

Analyse

0 2311 g Substanz gaben 0 5931 g CO_2 0 1492 g H_2O

Berechnet fur $C_{23}H_{26}O_4$ (normalen Ester)	$C_{16}H_{20}O$ (sauren Ester)	Gefunden
C = 70 36 %	69 02 %	69 99 %
H = 7 107 %	7 30 %	7 22 %

Die Entstehung eines Monobenzyl statt eines Dibenzyl esters ist kaum anders zu erklaren als durch sterische Hinderung

Drehung

S = 0 8044 g L (Ather) = 18 7124 p = 4 566
t = 17 d = 0 730 l = 1 dm α_D = +1 166
$[\alpha]_D$ = +34 7

7 Wochen spater

S = 0 6293 L (Ather) = 12 0401 p = 5 225
t = 13 d = 0 740 l = 1 dm α_D = +1 333
$[\alpha]_D$ = +34 0

G Natriumverbindung des Dimethyl bzw Diäthyl esters der α Dicarbonsäure und seine Zersetzungsprodukte

Darstellung der Natrium Verbindung

10 g Ester wurden in 20 ccm getrocknetem Ather gelost und die berechnete Menge (1 Mol) feinen Natrium drahtes hinzugesetzt Das Reaktionsgemisch wurde gelinde auf dem Wasserbade am Ruckflußkuhler bis zur Beendigung der Reaktion erwarmt (3—5 Stunden)

Versuch Athyl α Dicarbonsaure aus der Natriumverbindung des Dimethylesters darzustellen

Der oben beschriebenen Natriumverbindung wurde die $2^1/_2$ fache der berechneten Menge Athyljodid in atherischer Losung in kleinen Mengen durch den Kuhler zugesetzt und das Gemisch drei Stunden auf dem Wasserbade erhitzt Alsdann wurde Ather und uberschussiges Athyljodid abdestilliert, und der Ruckstand mit 100 ccm 5 %iger Natronlauge $^3/_4$ Stunde auf dem Wasserbade weiter erhitzt Ich hoffte dadurch den Ester zu verseifen und das Athylderivat der α Dicarbonsaure zu erhalten Da nach dem Erhitzen ein Ol auf der Flussigkeit schwimmen blieb, wurde, um dies zu entfernen Wasserdampf eingeleitet Es ging ein angenehm riechendes Ol uber, welches mit Semicarbazidlosung behandelt nach zweitagelangem Stehen ein Semicarbazon gab

Smp (aus Methylalkohol) 140—141

Da das Ol Kaliumpermanganatlosung sofort entfarbte, ist das Keton vermutlich ungesattigt Dieses Keton ist fur sich noch nicht weiter untersucht worden

Die aus dem Ruckstande gewonnene Saure erwies sich nicht als die gewunschte Athyl α Dicarbonsaure, sondern war ein optisch inaktives Ol

Die Verseifung hatte offenbar Ringsprengung hervorgerufen

Darstellung von Tanacetophoron aus der Natriumverbindung des Dimethylesters der α Dicarbonsaure

Um die interessanten Umwandlungen die in dem obigen Versuche stattgefunden hatten, weiter zu stu

dieren wurde in der folgenden Weise verfahren Zu einer Portion der oben beschriebenen Natriumverbindung des Dimethylesters der α Dicarbonsaure wurde zur Entfernung etwaiger Spuren von unverbrauchtem Natrium etwas Alkohol zugesetzt Nunmehr wurde etwas Wasser zugesetzt und das Gemisch einer Wasserdampfdestillation unterworfen Wie im vorigen Versuche ging ein angenehm riechendes Ol uber und das Destillat mit Semicarbazidlosung versetzt gab sofort ein Semicarbazon Wegen des Geruchs und der Enstehungsweise dieses Ketons wurde angenommen daß Tanacetophoron entstanden sei ein Keton das Semmler (Ber 33 277 (1900)) durch Destillation der α Dicarbonsaure mit Natronkalk erhalten hatte Um die Richtigkeit dieser Annahme zu prufen wurde das aus dem Ester dargestellte Keton mit dem durch Natronkalkdestillation gewonnenen sorgfaltig verglichen Dabei erwies sich daß beide Ketone in der Tat identisch waren daß aber das nach der neuen Methode dargestellte Keton unvergleichlich viel reiner als das durch Trockendestillation gewonnene war Erst nach zweimaliger Darstellung Umkrystallisation und Zersetzung des Semicarbazons des letzteren Ketons war es moglich ein Semicarbazon darzustellen das mit dem Semicarbazon des aus dem Ester gewonnenen Ketons vollkommen identisch war Da nach der neuen Methode die Ausbeute an Tanacetophoron uber 60 % der Theorie betragt empfiehlt sie sich zur Darstellung von reinem Tanacetophoron

Die folgende Tabelle gibt die gefundenen Konstanten fur das aus der Natriumverbindung des Dimethylesters der α Dicarbonsaure dargestellte Keton und sein Semicarbazon und die von Semmler (Ber 2, 3350)

fur das durch Trockendestillation der α-Dicarbonsaure uber Natronkalk gewonnene Tanacetophoron an

Keton aus der Natrium verbindung des Dimethylesters		Tanacetophoron (nach Semmler) Ber 25, 3350	
Sdp	215—217	Sdp	212—214
Sdp_{17-18}	99°	Sdp_{13}	89—90
$d_{19\ 15}$	0 9453	d_{20}	0 9378
n_D		n_D	1,4817

Geruch identisch

Semicarbazon	Tanacetophoron Semicarbazon
Krystallform Fett glanzende Blattchen	Fett glanzende Blattchen
Smp 187—188 (Zersetzung)	187—188 (Zersetzung)

Smp Gemisch von beiden Semicarbazonen 187—188

Analyse des Semicarbazons

0,1732 g Substanz gaben 0,3777 g CO_2, 0,1287 g H_2O

Berechnet fur Tanacetophoronsemicarbazon $C_9H_{15}N_3O$

C = 59,62 % Gefunden C = 59 47 %

H = 8,347 % H = 8,312 %

Der abgekuhlte Ruckstand wurde ausgeathert und dadurch ein optisch inaktives, neutrales Ol gewonnen

Sdp_{8-9} = 100—120

Nach dem Ausathern wurde der Ruckstand mit Schwefelsaure angesauert, nochmals ausgeathert, und das so gewonnene saure Ol mit Wasser und Tierkohle gekocht und filtriert Aus dem Filtrat schieden sich langsam zwei Sauren aus, die mechanisch getrennt werden konnten Die atherische Losung eines Gemenges beider Sauren erwies sich als optisch inaktiv

Diejenige Saure die in großerer Menge vorhanden war wurde aus Aceton und Wasser umkrystallisiert und schmolz bei 150—151 also neun Grad hoher als die α Dicarbonsaure Das Resultat der Analyse beweist aber unbedingt daß diese Saure mit der α Dicarbonsaure isomer ist also liegt hier wahrscheinlich racemische α Dicarbonsaure vor Bekanntlich schmilzt ja das racemische Gemisch einer optisch aktiven krystallisierbaren Substanz gewohnlich hoher als die beiden aktiven Formen[1]) Vermutlich wurde der Dimethylester der α Dicarbonsaure in der heißen konzentrierten alkalischen Losung verseift und fand gleichzeitig die Racemisation statt Das Atznatron kann hier wie in so vielen anderen Fallen beschleunigend auf die Racemisierung gewirkt haben Nur Spaltungsversuche konnen dieses interessante Problem losen

Die andere Saure die in kleinerer Menge vorhanden war krystallisierte in ausgepragten zugespitzten dicken Prismen

Smp 116—117

also identisch mit der β Dicarbonsaure (Ber 30 432)

Nach Semmler (Ber 30 439 (1897)) beruht die Entstehung von Tanacetophoron aus α Dicarbonsaure bei der Destillation mit Natronkalk auf der Umwandlung von α Dicarbonsaure in β Dicarbonsaure die nunmehr unter Kohlensaureabspaltung eine innere Kondensation nach dem folgenden Schema eingeht

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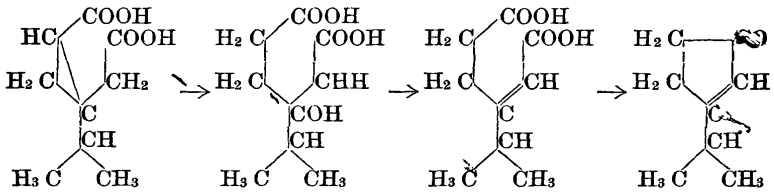
1) Nähere s Wallach Terpene und Campher S 158 und Landolt l c S 73



α Dicarbonsaure — Zwischenprodukt Instabil — β Dicarbonsaure — Tanacetophoron

Der Vorgang in dem obigen Falle kann in derselben Weise erklart werden, nur muß, um die Entstehung der Dicarbonsaure Smp 150—151 zu erklaren, Racemisation der aktiven Saure oder ihres Esters stattfinden

Als Einwand gegen diese Hypothese ist aber zu erwahnen

1) Die durch Verseifung des Dimethylesters erhaltene Saure zeigt keine Racemisation

2) α Dicarbonsaure mit 10 %iger Natronlauge $1^1/_2$ Stunden gekocht zeigte keine Racemisation

Die Zahlenangaben fur die Saure Smp 150—151 sind folgende

Analyse

0,1171 g Substanz gaben 0,2492 g CO_2, 0 0810 g H_2O

Berechnet fur $C_9H_{14}O_4$ C = 58,03 % H = 7,58 %

Gefunden C = 58,04 „ H = 7,73 „

Silbersalz

0 1172 g Salz gaben 0 0634 g Ag

Silber = 54,09 %

Berechnet fur $C_9H_{12}O_4Ag_2$ = 53,97 „

Die Hauptergebnisse der vorliegenden Arbeit sind folgende

1) Ein fester und ein flussiger Methylthujylalkohol (Homothujylalkohol) sind dargestellt worden In beiden Alkoholen ist wie im Thujylalkohol der Dreiring gegen verdunnte (5 %ige) Schwefelsaure bei gewohnlicher Temperatur bestandig Die drei nach t höheren Homologen dieser Alkohole sind Flussigkeiten

2) α Thujaketosaure zersetzt sich mit verdunnter Salzsaure gekocht unter Bildung eines ungesattigten Kohlenwasserstoffs der seinem Geruch und Siedepunkt nach dem Hydropseudocumol sehr nahe steht Gleichzeitig entstehen Sauren oder eine Saure deren Konstitution noch nicht festgestellt ist

α Thujaketosaure bildet je nach der Darstellungsmethode zwei Oxime, die in Bezug auf Schmelzpunkt und Drehung verschieden sind

3) Die aus der α Thujaketosaure durch Oxydation erhaltliche α Dicarbonsaure (Tanacetondicarbonsäure) ist gegen Kochen mit verdunnter Salzsaure oder Natronlauge ganz bestandig

4) Dimethyl Diathyl Di n propyl Diisobutyl Diisoamyl und Monobenzylester der α Dicarbonsaure sind dargestellt und bezuglich ihres optischen und chemischen Verhaltens untersucht worden Die molekulare Drehung die er Reihe zeigt ein deutliches Minimum

5) Der Dimethyl und Diathylester geben eine Natriumverbindung deren Zerfallsprodukte Tanacetophoron α Thujaketosaure und eine unbekannte optisch inaktive Dicarbonsaure Smp 150—151 sind

6) Das Anhydrid der α Dicarbonsaure reagiert leicht mit Ammoniak Anilin und Piperidin Ein Monamid der α Dicarbonsaure ist isoliert worden

7) Die Drehung konstanten der folgenden Substanzen sind zum ersten Mal untersucht worden

Methylthujylalkohol (fester und flussiger) Oxymethylenthujon

Oxim, Semicarbazon und Ammoniumsalz der α Thujaketosaure

Sechs Ester der α Dicarbonsaure Saures und normales Ammoniumsalz der α Dicarbonsaure

Ammoniumsalz des Monamids der α Dicarbonsaure

GT No 26

File No 480-09
Serial No 3

Diary No of letter replied to 8235

*No C 1468 23/6/10.

General and Revenue Secretariat
( )
the 190

To The First Asstt Resident

Date of issue 23 6 1910

Signed by

Sir,

I am directed to state that the Durbar propose to appoint an Englishman Mr Francis Usher, B Sc, as Professor of Chemistry, Central College, Bangalore and to request that you will be so good as to obtain the sanction of the Govt of India to his appointment at an early date.

SUBJECT

2. Particulars regarding the terms of the appointment are given in the accompanying Statement.

Yours etc

[illegible]
18/6/10

For Secy

[illegible]
15/7/10

[illegible]

List of enclosures

Copied by

Examined by

GPB—10,000—20 4 06

Particulars of information to accompany the ~~Dunbar~~ application by the Dunbar for the sanction of the Govt of India, regarding any European other than an official in the Service of Govt in British India, whom it is proposed to employ in the Mysore State

Name.	Frances Usher
Age	24 years
Nationality	English
Nature of proposed employment	Professor of Chemistry in the Central College on probation for 5 years
Qualifications	B Sc, London, Honours in Chemistry with Physics as Subsidiary Subject, 1906.
Proposed Salary and Pension, if any	Rs 500 rising to Rs 1000 by annual increments of Rs 50 The Service is pensionable under the Mysore Service Regulations
Previous employment and Salary	Nil

(with this exception viz that the rate of exchange of pension will be the same as that fixed for members of the Indian Educational Service)

~~Pension~~

~~Reference~~

Pension if any, received from the British Govt } Nil

References if any — ~~To~~ Sir William Ramsay, K C B, F R S, Professor of Chemistry, University College, London.

Remarks Nil

18/6/10

For Offg Secy

18/6/10

Offg Secy

IV [illegible] 1/7

[illegible] D 41

No 3978

480-09-4

Pol 9 54

dt 1-7-10

FROM

MAJOR W G GREY I A
FIRST ASSISTANT TO THE RESIDENT IN MYSORE

To

The Dewan of Mysore

Dated Bangalore, 1st July 1910

SIR

With reference to Mr Balasundaram Iyer's letter No C 140-Pol, dated the 23rd June 1910 I am directed to state that there is no objection to the appointment of Mr Francis Usher, B Sc as Professor of Chemistry Central College Bangalore

I have the honour to be
Sir,
Your most obedient servant,

W G Grey Major,
First Assistant Resident

35

GRS 28]

File No 480-09
Serial No 357

Diary No of letter replied to 41

Proceedings of the Government of His Highness the Maharaja of Mysore

GENERAL AND REVENUE SECRETARIAT
( )

the 19

Date of issue

Signed by

ORDER THEREON No

READ— Letters No 11437/819 and 11600/837 by the 25th to 30th May 1910 respectively from the Dr of Coorg in Mysore recommending the appointment of Mr Francis Usher, B.Sc., as Professor of Chemistry, Central College, Bangalore

2 Correspondence ending with letter No 3978 by the 1st

over

SUBJECT

-6

July 1910 from the First Assistant to the Resident in Mysore stating that there is no objection to the employment of Mr. Usher ~~on the~~ as Professor of Chemistry

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Order thereon

No C 23-24 Camp Mysore,
Edu 480-09. 13th July 1910

Govt are pleased to sanction the appointment of Mr. Francis Usher, B. Sc, as Professor of Chemistry, Central College, Bangalore, on the following terms.

(1) ~~Pay~~ His pay will be fixed at Rs 500 rising to 1000 by annual increments of Rs 50

(2) The appointment will be ~~to be~~ on probation for 5 years,

G.A.S 27]

GENERAL AND REVENUE SECRETARIAT

(Continuation Sheet draft form)

at the end of which period it will be open to Govt or to Mr Usher to terminate the engagement.

3). He will be given single first class passage and railway fare from London to Bangalore, and if the engagement is terminated by either party at the end of 5 years, for the return journey also

4) The leave rules will be those contained in the Mysore Service Regulations.

5) Travelling allowances will be the same as for Govt officers of class A_{II} for the first 5 years and of class A_{I} thereafter

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b) Pension will be regulated by the rules in the Imperial Service Regns

4) The rate of exchange of pension and leave allowances will be the same as that fixed for members of the Indian Civil Service in British India

2 The Govt ~~is requested~~ to will communicate the above orders to Mr Usher and request him to join duty as early as practicable.

Hon
12 July

8/7/10

8/7/10 For Secy

9/7/10

To The Govt of Goa

n from Further Intro Par

8/7/10

IV Hour 17

No. 3978.

Pol: 9

Dt 1-7-10

Edn 480-09-4

FROM

MAJOR W. G. GREY, I. A.,
FIRST ASSISTANT TO THE RESIDENT IN MYSORE.

To

The Dewan of Mysore.

Dated Bangalore, 18th July 1910

SIR,

With reference to Mr. Balasundaram Iyer's letter No.C.146-Pol., dated the 23rd June 1910, I am directed to state that there is no objection to the appointment of Mr. Francis Usher, B.Sc., as Professor of Chemistry, Central College, Bangalore.

I have the honour to be,
Sir,
Your most obedient servant,

W. G. Grey Major,
First Assistant Resident.

K.M.

R. P. B.—6-1910.—500

GRS 27]

GENERAL AND REVENUE SECRETARIAT

Zr 245 / 25/10 Handed

(Continuation Sheet draft form)

Notify the Director

No 3385 / EDn 480-09-1 18 10 10

Mr. Francis Usher, B Sc ~~has been~~ is appointed Professor of Chemistry in the Central College, Bangalore with the effect from the 25th Sept 1910. ~~(inclusive)~~

By order

Published at page 421 of Pt-I of the Gazette of 20 10 10

Dr 264 / 11 10 10

Dr / 8/10/10

For Secy 7/10/10

Dr 6/10/10 Secy 7/10/10

To the Computer, Mysy for publication in the Gazette

Mw 6/10/10

3386 Copy to Comptroller with the remark that Mr Usher's salary upon his duties on the foregoing date

MGCLD—30 000—5 10

Zr 15/10 15/10

25 Sept 10

Bryden

[illegible]

[illegible]

5 To the Govt of Edn & Compltr, Govt No C 23-24 dt 13 7 10

Sanctions the appointment of Mr Usher as Professor of Chemistry in the Central College

6 From the Govt of Edn, No 3302/225 dt 28 9 10

Reports that Mr Usher joined his appointment as Professor of Chemistry on the forenoon of Sunday the 25th Septr, 1910

7 } Notification No 3385 dt 18 10 10 Notifies the appointment of Mr Francis Usher, B Sc, as Professor of Chemistry in the Central College, Bangalore, with effect from the 25th Septr 1910